PATENT ABSTRACTS OF JAPAN

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(54) MAGNETIC PARTICLE POWDER FOR MAGNETIC TONER AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To increase an electrostatic charge quantity with a negative polarity and to improve the dispersibility and wettability in a resin by adhering a silicon compd. of specific quantity to the iron of particle surfaces and specifying the electrostatic charge quantity.

SOLUTION: The water-soluble silicon compd. is added in the amt. at which the content of silicon attains 0.1 to 5.0 wt.% of the iron into an alkaline suspension of pH ≥12 after the formation of magnetic particles and is controlled to the pH value of the desired region by hydrochloric acid, by which the silicon component is adhered to the surface parts of the magnetic particles. As a result, the magnetic particles normally having the positive polarity eventually exhibits negative polarity. The electrostatic charge quantity of this magnetic particle powder is -60 to -10 μc/g, more preferably -50 to -15 μc/g, further preferably -5 to -10 μc/g. When the powder is used for magnetic toners, the outside contour parts and surface parts of the magnetic toners have the negative charge polarity and since the magnetic powder has the large electrostatic charge quantity, high development characteristics are continuously and stably obtd. without increasing the reverse polarity and weak electrostatic charge toner particles. The image characteristics having the high image quality are thus obtd.

CLAIMS

[Claim(s)]
[Claim 1]To a particle surface, it is iron (Fe). It receives and is silicon (Si). It carries out. Magnetic particle powder for magnetic toner which 0.1 to 5.0% of the weight of a silicon compound has adhered, and is characterized by electrification quantity being -60 - -10microc/g.
[Claim 2]A manufacturing method of magnetic particle powder for magnetic toner adding a water-soluble silicon compound, making pH or less into eight after an appropriate time, and making a silicon compound adhere to the surface of the magnetic particle powder concerned after pH uses magnetite particle powder as 12 or more alkaline suspension.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to magnetic particle powder for the magnetic toner used for the development of the one-ingredient methods a xerography, an electrostatic recording method, for xerography, etc., and a manufacturing method for the same.
It is related with magnetic particle powder which was suitable as an object for magnetic toner used for the development system using a digital latent image in more detail, and a manufacturing method for the same.

[0002]
[Description of the Prior Art]The magnetic toner in which the development system of the dry type copying machines the conventional xerography, an electrostatic recording method, for electrostatic copiers, etc. has straight polarity is adopted widely. It is because a cheap developer is made with ** compact with easy needlessness and ** toner reinforcement for ** concentration control with easy ** maintenance with good ** image reproducibility as a reason the one-ingredient development system by these dry type copying machine is adopted widely. However, if the intermediate color which what (reappearance of intermediate color) a photograph is faithfully reproduced for is needed, and is expressed by the difference in the density of a line does not always have the the same thickness of a line, the sharpness of imaging quality including fine line reproducibility, story tonality, resolution, image concentration, etc. will pose a problem especially in recent years. Reappearance, resolution, etc. of story tonality satisfied the above-mentioned advanced demand, and made the stably same intermediate color the method which carries out a reappearance output, it changes to the conventional analog form, the thing using a digital latent image is developed, and the copying machine itself came to be written minutely [there is no latent image until now and]. As those copying machines, a laser beam printer (LBP), a digital printer (PPC), etc. are raised, These are selenium (Se). It is a thing using photo conductors, such as an organic photoreceptor (OPC) of an amorphous silicon (a-Si) and right charge, and since such surface polarity has straight polarity, as for magnetic toner, the thing of a negative polarity toner is used. However, the magnetic powder particles used for these magnetic toner, Many generally have straight polarity and there is a problem referred to as having to control the strength (electrification quantity) of the polarity and polarity of magnetic toner to negative polarity in using it for the raw material for magnetic toner of negative polarity in manufacture of magnetic toner using a charge controlling agent. In the manufacturing process of a toner, the manufacturing method of common magnetic toner Magnetic particle powder, After it dries the massive object which made carry out specified quantity mixing of binding resin, a charge controlling agent, the colorant, etc., and was acquired by carrying out melt kneading and mechanically ground means, such as a jet mill, grind (pulverizing method), usually it classifies and manufactures to the particles of a prescribed particle size. In order to manufacture negative magnetic toner at this time, polarity and electrification quantity are controlled and manufactured to an appropriate value by charge controlling agents, such as a metallic complex and azo dye. However, as for conventional magnetic toner, particle shape and a surface state, the character of a powder surface, and the interaction between granular materials are regarded as

questionable. for example, the wettability [on the state of magnetic particle powder and binding resin where it was kneaded, and as opposed to this magnetic powder particle] (binding capacity of magnetic particle powder and resin) of resin and the dispersion state in the inside of resin – it is bad (condensation). When ground by the above-mentioned grinding means, bordering on the portion on the surface of magnetic particle powder, or the part of a between [resin], separation cutting is carried out and it is ground in many cases (destructive cutting). If the dispersibility in the inside of resin and wettability manufacture using bad magnetic particle powder, the filling factor of magnetic powder material which receives per magnetic toner particle piece will not become uniform, but, as a result, variation will be produced in the magnetic action of magnetic toner each, and the inconvenience of reducing a developing characteristic will be produced. The surface where destructive cutting of the magnetic toner ground with pulverizing method was carried out has intense unevenness, therefore since the mobility of magnetic toner worsens, it is easy to produce the condensation and solidification between magnetic toner, and it becomes a cause by which the sharpness of imaging quality is missing, including fine line reproducibility, story tonality, resolution, copy density, etc. Therefore, it is common to carry out hot blast stove ****** of the magnetic toner ground for the purpose of raising the mobility of magnetic toner, to fuse the surface of magnetic toner, and to perform treatment taken a spherical shape. Although the mobility of magnetic toner itself improves by performing such processing, in order that magnetic toner may control and manufacture polarity and electrification quantity to an appropriate value by a charge controlling agent, the structure of the color as a charge controlling agent is complicated, It is lacking in stability, and decomposes or deteriorates at it from those, such as treatment temperature conditions in the time of heat kneading, a mechanical shock, and friction, It is influence of producing the phenomenon in which electrification controllability falls, or the outline part and surface part of a negative polarity toner having much conventional straight polarity magnetic particle powder, and the thickness of a resin coating layer becoming uneven etc., namely, the magnetic toner of reverse polarity and the mixing ratio of weak electrified toner particles increase. In order to consider it as magnetic toner excellent in improvement in imaging quality, fine line reproducibility, and story tonality, Since it is known that it is so effective that the diameter of a granule is used, it is necessary to make magnetic toner diameter[of a granule]-ize. It becomes a tendency which increases further and the standup of frictional electrification becomes blunt, the problem of an offset phenomenon, toner scattering, dirt inside the plane, etc., etc. occur, and the magnetic toner of reverse polarity and the mixing ratio of weak electrified toner particles become the big cause of reducing a picture characteristic. Therefore, as magnetic toner needed with an one-ingredient development system in order to reproduce a photograph faithfully, To meet a demand of a detailed latent image and fine line reproducibility, and story tonality, it can respond to improvement in the speed with the diameter of a granule, Although research of the magnetic toner which can respond and which has negative polarity with the diameter of a granule, and development are wholeheartedly considered by the severe demand of highly-efficient-izing of high-definition-izing etc., quality improvement, etc. and it is developed, what is still satisfied does not exist.

[0003]

[Objects of the Invention]Electrification quantity of this invention is also large at negative polarity, and an object of this invention is to provide magnetic particle powder and a manufacturing method for the same excellent also in the dispersibility in the inside of resin, or wettability.

[0004]

[Means for Solving the Problem]Particle shape and a surface state which are required of magnetic toner of negative polarity, this invention persons, A fault of an interaction between granular materials, such as a dispersion state between particles and character of a powder surface, is made solved, That manufacture of magnetic particle powder for magnetic toner which has negative polarity should be attained, Each pH value and silicon (Si) of a specific silicate A result of having examined coating weight and electrified polarity wholeheartedly, It has the characteristic suitable for magnetic toner of negative polarity, the knowledge of the manufacturing method of magnetic particle powder which has negative polarity with the sufficient wettability (binding capacity of magnetic particle powder and resin) of resin to magnetic powder particles and a dispersion state in inside of resin is carried out, and it came to complete this invention. That is, this invention is iron (Fe) to a particle surface. It receives and is silicon (Si). It carries out. 0.1-5.0 A silicon compound of weight % has adhered, And magnetic particle powder for magnetic toner, wherein electrification quantity is -60 - -10microc/g, After pH uses magnetite (Fe_3O_4) particle powder as 12 or more alkaline suspension, It is a

manufacturing method of magnetic particle powder for magnetic toner adding a water-soluble silicon compound, making pH or less into eight after an appropriate time, and making a silicon compound adhere to the surface of the magnetic particle powder concerned. Silicon (Si) used for this invention Silicon (Si) It is used in a form of a compound, For example, it is not what can mention oxides, such as hydroxide, such as silicate, such as Na_2SiO_3 and Na_2SiO_5, and $Si(OH)_4$, and SiO_2, etc., and is limited to especially these, When the pH of solution is 12 or more, what is necessary is just water solubility.

[0005]

[Embodiment of the Invention]Hereafter, the manufacturing method of the magnetic particle powder about this invention is explained in full detail. Namely, the inside of the stirring type oxidation reaction tub of the wet type in which magnetic particle powder generally has a gas vent pipe, After heating the suspension containing the ferrous hydroxide colloid produced by mixing a ferrous salt aqueous solution and an alkaline aqueous solution while nitrogen replaced at 70 to 100 **, It changes from nitrogen to oxygen containing gas, such as air, is manufactured by blowing gas, and is manufactured through processes, such as filtration, washing, desiccation, and grinding, after that by the conventional method. The particle shape generated by such a wet reaction turns into n face piece, an unfixed type, and spherical shape with the kind and quantity of the alkali solution used for neutralization.

[0006]After the ending reaction which made the magnetic particle generate by the above-mentioned method, and in pH 12 or more alkaline suspension, a water-soluble silicon compound (for example, specific silicate (Na_2O-$nSiO_2$)) -- silicon (Si) content -- iron (Fe) Receive. it becomes 0.1 to 5.0 % of the weight -- quantity addition being carried out and, After carrying out stirring mixing for a while, the magnetic particle which should usually have straight polarity comes to show negative polarity according to making the pH value (pH 5 or less [pH eight or less preferably]) of the field made into the purpose with chloride adjust, and making a silicon component adhere to a magnetic particle surface part. When not carrying out pH adjustment even to this field, it is still a magnetic particle which has straight polarity. What is necessary is just to make the amount of silicon of a magnetic-particle-powder surface part increase, in order to enlarge negative band electrical quantity of the magnetic particle powder produced by performing it above. The making the coating weight of silicon in a specific silicate increase at this time purpose, a specific silicate is added in pH 12 or more [of an after / ending reaction] alkaline suspension, the divalent metal ion (Mn^{2+} and Co^{2+}.) after carrying out stirring mixing for a while Zn^{2+}, nickel^{2+}, Mg^{2+}, Cu^{2+}, etc., The pH value of the field which is independent, or targets the slurry solution of the system of reaction with a hydrochloric acid aqueous solution after carrying out stirring mixing in two or more kinds of combination may be made to adjust a water-soluble pigment agent, a coupling agent, etc., and a magnetic-particle-powder surface part may be made to carry out coprecipitation adhesion of the silicon. It does not limit in particular for those amount used. The magnetic particle powder which made the silicon component adhere to a magnetic-particle-powder surface part by such a method, considered it as the product of this invention through processes, such as filtration, washing, desiccation, and grinding, after that with the conventional method, and was manufactured turns into magnetic particle powder which has negative polarity.

[0007]The electrification quantity of the magnetic particle powder of this invention is -60 - -10microc/g, and is -50 - -15microc/g preferably, Since it is -50 - -20microc/g preferably and is the magnetic powder whose electrification quantity is [that the outline part and surface part of magnetic toner have negative band electrode nature] large, when it uses for magnetic toner, Neither reverse polarity nor weak electrified toner particles increase, a high developing characteristic will be acquired by being stabilized continuously, and a high-definition picture characteristic will be obtained. In this case, the target electrification quantity is not obtained on developer support as electrification quantity is more than -10microc/g, but the sharpness of the first stage to a picture worsens, and since it is lower than an appropriate range, image concentration serves as a thin picture with much fogging. The evil which it becomes easy to produce the so-called charge-up phenomenon of the magnetic toner which the electrification quantity of a developer is accumulated, becomes still larger, and checks proper electrification quantity by carrying out by repeating image output as it is less than -60microc/g, and produces the fall of image concentration gradually especially under damp low temperature environment occurs.

[0008]The measuring method of the electrification quantity of the magnetic particle powder of this invention is as follows. namely, -- using the Toshiba Chemical CORP. make blowing off granular material electrification measuring device --

first – a 100-ml poly bottle – the ferrite carrier 97.0g of Cu-Zn, and magnetic particle powder 3.0 g (3% of content), [put in and] Mixed elegance which rotated for 5 minutes and was made to DEBE-ize at 110 rpm Right weighing of the 0.2 g was carried out, and the electrification quantity of a value and a 30-second value was measured for 10 seconds by ** of nitrogen gas 1 kg/cm^2.

[0009]In the state of this magnetic particle powder and binding resin where it was kneaded, since magnetic powder is contained 30 to 80% of the weight to the whole magnetic toner, influence the performance of magnetic toner greatly, and. If the wettability (binding capacity of magnetic particle powder and resin) of resin to this magnetic particle powder and the dispersion state in the inside of resin are bad, in order to worsen the magnetic toner characteristic like the above, Although mobility was measured with the pouter tester device by Hosokawa Micron CORP. and the magnetic particle powder of this invention was converted into the weight per minute (g/min), Since mobility is also improving rather than elegance conventionally, even if it makes it the small grain diameter toner needed for the demand of highly-efficient-izing or quality improvement, inside magnetic toner, Since the magnetic powder particles which have straight polarity are not used, magnetic particle powder with large electrification quantity is contained in the outline part and surface part of magnetic toner by negative polarity, Even if it produces the phenomenon in which decompose or deteriorate by the treatment temperature conditions in the time of heat kneading of the influence of the thickness of a resin coating layer becoming uneven etc., or the color as a charge controlling agent, a mechanical shock, friction, etc., and electrification controllability falls, From becoming easy [manufacturing process management], since the mixing ratio of reverse polarity or weak electrified toner particles does not increase, and excelling also in wettability or dispersibility. The magnetic action of magnetic toner each becomes uniform. As a result, even if it increases content, electrostatic property, image concentration, fogging, etc. and toner scattering will not be caused, and a clear copied image will be obtained. From being made to the diameter of a granule, magnetic toner can also follow enough a detailed latent image and fine line reproducibility, and story tonality, and can respond to improvement in the speed, and the magnetic toner which also meets the severe demand of highly-efficient-izing of high-definition-izing etc., quality improvement, etc. can be provided.

[0010]Dispersibility to the inside of resin of the magnetic particle powder which has the negative polarity of this invention, and magnetic toner evaluation were performed by the following method. namely, – as magnetic powder 40 weight section and binder resin – polyester resin (the product made from Kao Atlas.) After mixing enough molecular weight abbreviation 5000 59 weight section and carbon black (Mitsubishi Chemical make, MA-100) 1 weight section with a Henschel mixer together, Carry out melt kneading, carry out cooling solidification with a heating type biaxial mixer, and with a jet mill type grinder and a classifier. After obtaining the magnetic toner of the negative polarity which has the mean particle diameter of 10 micrometers, the magnetic distribution of this magnetic toner was measured by the following brush dispersing method about this magnetic toner using what improved the developing box of the commercial one component system copying machine. the brush dispersing method – a mug – when the number of rotations of a roller is improved at a variable ceremony and the charge of magnetic toner is made to fixed-ize, it is making number of rotations quick, and the toner with weak magnetism (magnetic material content – few) is flown with a centrifugal force. By measuring the flown quantity and magnetism of the toner, it is the method of measuring the dispersibility of the magnetic powder in magnetic toner.

[0011]That is, since the above-mentioned brush dispersing method differs in the magnetic force of each magnetic toner when the dispersibility of the magnetic powder particles to the inside of resin is bad, it is an instrumentation method using magnetic toner with weak magnetic force being flown early. Measurement of toner scattering the suction pipe of PARTICLE COUNTER made from RION (KC-03 **** type particle counter), attaching to the developing box upper part for two ingredients, and putting in magnetic toner in a box – a mug – a roller being rotated violently and according to the centrifugal force by the rotation. As a result of attracting dust particles and measuring magnetic toner particle diameter and the number from the toner scattering atmosphere in a box, the amount of scattering (dust) of magnetic toner was a thing of ultralow volume.

[0012]As a result of carrying out various kinds of measurement using an aforesaid measuring method, the magnetic particle powder of this invention, In the state with binding resin for magnetic toner where it was kneaded, wettability (binding capacity of magnetic particle powder and resin) with resin and the dispersion state in the inside of resin are

good, The content and the filling factor of magnetic particle powder become uniform, and magnetic toner with the diameter of a granule Reverse polarity, From the mixing ratio of weak electrified toner particles being very very small, and the electrification quantity of the standup of frictional electrification being well stable further. The clear copied image was obtained without reducing a picture characteristic, since the characteristic of imaging quality is raised, and there is also no toner scattering including copy image quality, resolution, image concentration, etc., and the problem of an offset phenomenon, dirt inside the plane, etc., etc. were prevented.

[0013]As the characteristic for which magnetic particle powder is asked, for the demand of highly-efficient-izing of magnetic toner used for various kinds of [in recent years] xerography systems, ** Although it is called for that the good thing (a toner characteristic becomes uniform) of dispersibility and ** saturation magnetization are large (the conveyance nature of magnetic toner is good), that ** residual magnetization is low (transfer nature is good), that ** black degree is large (image concentration is good), etc., Since the magnetic particle powder of this invention has polyhedral form (the shape of a ball also moving aside), its dispersibility is also good, Since magnetic shape anisotropy is small, holding power (Hc) is small, and in connection with it, residual magnetization (sigmar) is also small, The particle size distribution of this magnetic body for saturation magnetization (sigmas) being large magnetic particle powder, and also filling the aforementioned demand, it is good that it is 0.5 micrometer or less – holding power (Hc) becoming small too much, and, if 0.5 micrometer is exceeded. In connection with it, residual magnetization (sigmar) becomes still smaller, the tinting strength of what improving declines, if the content of magnetic particle powder is increased, a fixing defect will be started, picture nature and transfer nature will get worse, and dispersibility will worsen the whole characteristic. Therefore, it is desirable. It is good that it is 0.3-0, and 20 micrometers that it is 0.4-0.15 micrometer at best especially preferably. Since residual magnetization (sigmar) also becomes still larger in connection with [become / holding power (Hc) / that it is under 0.15 micrometers or more / too much / large] it, Since distribution in binding resin becomes difficult and remains as an aggregate that it is easy to condense magnetic particle powder, inferior transfer and a fine line reproducibility fall arise, and high resolution is no longer obtained. About the determination of a particle size, it is required to provide the demand of highly-efficient-izing for which the magnetic toner for one ingredients by each manufacture is asked in the appropriate range filled enough.

[0014]

[Example]Although an example and a comparative example are given and the manufacturing method of the magnetic particle powder of this invention is explained concretely hereafter, this invention is not limited to this. First, the details of the manufacturing method of the magnetic particle powder for magnetic toner used for this invention are explained. First, 4 l. of pure water is put in, aerating nitrogen gas in a stirring type oxidation reaction container with a capacity of 15 l. which has a gas vent pipe, It is a 3.33 mol/l. ferrous salt aqueous solution in it. 1.2 l. is added, It ranks second. 2.0 mol/l. sodium carbonate solution 2.8 l. adds, After adding 2.0 l. of 2.0 mol/l. caustic soda aqueous solutions after carrying out stirring mixing for 30 minutes and considering it as whole volume, temperature up was carried out to 90 **, stirring, it was filtered and washed, and was dried and the output which aerated the air of 1 l. / min for 8 hours, and was made was pulverized.

[0015]As a result of checking with the Akashi Factory scanning electron microscope (SEM) photograph, the shape of magnetic powder particles the number of fields of a particle surface, Particle diameter of an enlargement With the polyhedron magnetite particles which exist ten or more as a result of surveying each number of fields of 100 pieces (I counted the surface which is visible at this time, and thought that that back side was also the same). The mean particle diameter draws the parallel lines of prescribed width, after expanding a SEM photograph with a copy machine, and it is the particles on the line. The particle diameter (horizontal Ferre) of 150 pieces is measured visually, As a result of **(ing) particle diameter for magnification and considering it as a pitch diameter as a particle diameter value, at 0.23 micrometer. Magnetic properties are vibrating sample magnetometers (Toei Industry VSH-1 type). As a result of using and measuring, the holding power (Hc) in 5KOe (oersted) is 60 Oe (oersted), and saturation magnetic flux densities (sigmas) are 86.5 emu/g and a residual magnetic flux density (sigmar). It was 5.5 emu/g. Specific surface area was 5.8m^2/g as a result of measuring by the full automatic surface area measuring device multi-soap made from Yuasa Eye Onyx marble.

[0016]. Were obtained with the reaction method explained with the details of the manufacturing method of the magnetic

particle powder of one to example 4 example. PH value which it has polyhedron particle shape in 12 or more ending reaction slurry solutions, receiving Fe_3O_4 in a sodium silicate solution – 1.25:2.5:5.0:10.0 wt% – it being made to add and, Stirring mixing is carried out for 15 minutes, and it is the above-mentioned reaction vessel. A 0.5N mol hydrochloric acid aqueous solution is added at the rate of 10 ml/min with a metering pump, and it is pH. Filter and wash it, it is dried, the sample adjusted to 8.0-5.0 is ground, and the processing condition and evaluation result which investigated electrification quantity, electrical resistance, and mobility are shown in Table 1. As shown in Table 1, it is silicon (Si) to iron (Fe). An increase of content checked that the electrification quantity of negative polarity increased.

[0017]PH value which has the polyhedron particle shape used for one to comparative example 2 Examples 1-4 stops addition of a sodium silicate solution in 12 or more ending reaction slurry solutions, and it is the last pH value. Other than having been referred to as 8.0 and 5.0, as a result of performing the same processing as the above, negative polarity was not shown.

[0018]The processing condition and evaluation result at this time are written together to Table 1.

[0019]

[Table 1]

	項　目	実施例 1	実施例 2	実施例 3	実施例 4	比較例 1	比較例 2
処理条件	スラリーPH	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量 (g)	50	50	50	50	50	50
	SiO_2添加量 (重量%)	1.25	2.50	5.00	10.0	無	無
	最終スラリー PH	8.0	5.0	5.0	5.0	8.0	5.0
	洗浄水 (市水,リットル)	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体
	Si/Fe付着量 (重量%)	0.76	0.98	1.29	3.95	極微量	極微量
	帯電量 (μc/g)						
	10sec	-16.0	-21.3	-25.8	-48.1	+13.3	+10.7
	30sec	-16.3	-21.0	-25.9	-49.0	+14.6	+11.0
	流動性(g/min)	18.6	21.6	27.6	24.4	13.4	17.0
	磁気特性 (1K Oe)						
	Hc	57	57	58	58	57	58
	σr	5.8	5.7	5.8	5.8	5.7	5.8
	σs	68.7	68.1	68.3	67.9	68.3	68.0
	電気抵抗 (Ω) 印加電圧 100V	1.3×10^{7}	6.8×10^{8}	4.5×10^{8}	3.7×10^{7}	9.2×10^{8}	6.8×10^{7}

[0020]PH value which it has the polyhedron particle shape used for five to example 9 Examples 1-4 in 12 or more ending reaction slurry solutions, receiving Fe_3O_4 in a sodium silicate solution 2.5wt% – the making the coating weight of silicon in a specific silicate increase (coprecipitation) purpose, after adding and carrying out stirring mixing for 15 minutes, a divalent metal ion (Mn^{2+}, Co^{2+}, Zn^{2+}, and nickel^{2+}.) After making the pigment agent and coupling agent of Mg^{2+}, Cu^{2+}, etc. and solution add and also carrying out stirring mixing for 15 minutes, a 0.5N mol hydrochloric acid aqueous solution to the above-mentioned reaction vessel with a metering pump. PH value It adjusts to 5.0 and grinds [filter, wash, dry and], and the processing condition and evaluation result which investigated electrification quantity,

electrical resistance, and mobility are shown in Table 2. As shown in Table 2, when a divalent metal ion etc. and water-soluble pigment agent, and the coupling agent were added, the content of silicon (Si) began to increase to iron (Fe), and it was checked that electrification quantity also increases. Those sulfate, a chloride, a nitrate, etc. can be mentioned as a divalent metal ion source.

[0021]As a result of performing the same processing as the above except having stopped addition of the sodium silicate solution by three to comparative example 4 Examples 5-9, the polarity of magnetic particle powder did not change from positive to negative. It is written together to Table 2 that an evaluation result is a processing condition at this time. As the above-mentioned example showed, all in an ending reaction slurry solution a sodium silicate solution, In order to become the magnetic particle powder in which negative polarity is shown as a result of filtering, washing, drying and cracking and measuring electrification quantity, after making PH value into an acid side by chloride neutralization, and to enlarge electrification quantity, What is necessary is just to make the amount of silicon of the outline part of magnetic particle powder, or a surface part increase, and a divalent metallic ion, a water-soluble pigment agent, a coupling agent, etc. may be added, and silicon may be made to coprecipitate further.

[0022]

[Table 2]

	項　目	実施例5	実施例6	実施例7	実施例8	実施例9	比較例3	比較例4
処理条件	スラリーPH	12.5	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量 (g)	50	50	50	50	50	50	50
	SiO_2添加量 (重量%)	2.50	2.50	2.50	2.50	2.50	無	無
	$MnCl_2$(重量%)	1.00	無	無	無	無	1.00	無
	$ZnCl_2$(重量%)	無	1.00	無	無	無	無	無
	$MgCl_2$(重量%)	無	無	1.00	無	無	無	1.00
	顔料　分散剤 (重量%)	無	無	無	1.00	無	無	無
	カップリング剤 (重量%)	無	無	無	無	1.00	無	無
	最終スラリーPH	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	洗　浄　水 (市水,リットル)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体	多面体
	Si／Fe付着量 (重量%)	1.07	1.06	0.96	0.91	1.05	極微量	極微量
	帯電量 (μc/g)							
	10sec	-22.2	-20.3	-23.9	-29.0	-30.4	+7.4	+1.1
	30sec	-22.6	-21.7	-25.3	-31.2	-31.4	+7.9	+1.2
	流動性(g/min)	22.8	23.8	20.4	24.3	25.0	13.9	13.0
	電気抵抗 (Ω) 印加電圧 100V	1.1×10^{7}	5.2×10^{7}	5.6×10^{7}	3.8×10^{7}	3.0×10^{8}	3.5×10^{8}	5.8×10^{7}

TECHNICAL FIELD

[Field of the Invention]This invention relates to magnetic particle powder for the magnetic toner used for the development of the one-ingredient methods a xerography, an electrostatic recording method, for xerography, etc., and a manufacturing method for the same.

It is related with magnetic particle powder which was suitable as an object for magnetic toner used for the development system using a digital latent image in more detail, and a manufacturing method for the same.

TECHNICAL PROBLEM

[Description of the Prior Art]The magnetic toner in which the development system of the dry type copying machines the conventional xerography, an electrostatic recording method, for electrostatic copiers, etc. has straight polarity is adopted widely. It is because a cheap developer is made with ** compact with easy needlessness and ** toner reinforcement for ** concentration control with easy ** maintenance with good ** image reproducibility as a reason the one-ingredient development system by these dry type copying machine is adopted widely. However, if the intermediate color which what (reappearance of intermediate color) a photograph is faithfully reproduced for is needed, and is expressed by the difference in the density of a line does not always have the the same thickness of a line, the sharpness of imaging quality including fine line reproducibility, story tonality, resolution, image concentration, etc. will pose a problem especially in recent years. Reappearance, resolution, etc. of story tonality satisfied the above-mentioned advanced demand, and made the stably same intermediate color the method which carries out a reappearance output, it changes to the conventional analog form, the thing using a digital latent image is developed, and the copying machine itself came to be written minutely [there is no latent image until now and]. As those copying machines, a laser beam printer (LBP), a digital printer (PPC), etc. are raised, These are selenium (Se). It is a thing using photo conductors, such as an organic photoreceptor (OPC) of an amorphous silicon (a-Si) and right charge, and since such surface polarity has straight polarity, as for magnetic toner, the thing of a negative polarity toner is used. However, the magnetic powder particles used for these magnetic toner, Many generally have straight polarity and there is a problem referred to as having to control the strength (electrification quantity) of the polarity and polarity of magnetic toner to negative polarity in using it for the raw material for magnetic toner of negative polarity in manufacture of magnetic toner using a charge controlling agent. In the manufacturing process of a toner, the manufacturing method of common magnetic toner Magnetic particle powder, After it dries the massive object which made carry out specified quantity mixing of binding resin, a charge controlling agent, the colorant, etc., and was acquired by carrying out melt kneading and mechanically ground means, such as a jet mill, grind (pulverizing method), usually it classifies and manufactures to the particles of a prescribed particle size. In order to manufacture negative magnetic toner at this time, polarity and electrification quantity are controlled and manufactured to an appropriate value by charge controlling agents, such as a metallic complex and azo dye. However, as for conventional magnetic toner, particle shape and a surface state, the character of a powder surface, and the interaction between granular materials are regarded as questionable. for example, the wettability [on the state of magnetic particle powder and binding resin where it was kneaded, and as opposed to this magnetic powder particle] (binding capacity of magnetic particle powder and resin) of resin and the dispersion state in the inside of resin – it is bad (condensation). When ground by the above-mentioned grinding means, bordering on the portion on the surface of magnetic particle powder, or the part of a between [resin], separation cutting is carried out and it is ground in many cases (destructive cutting). If the dispersibility in the inside of resin and wettability manufacture using bad magnetic particle powder, the filling factor of magnetic powder material which receives per magnetic toner particle piece will not become uniform, but, as a result, variation will be produced in the magnetic action of magnetic toner each, and the inconvenience of reducing a developing characteristic will be produced. The surface where destructive cutting of the magnetic toner ground with pulverizing method was carried out has intense unevenness, therefore since the mobility of magnetic toner worsens, it is easy to produce the condensation and solidification between magnetic toner, and it becomes a cause by which the sharpness of imaging quality is missing, including fine line reproducibility, story tonality, resolution, copy density, etc. Therefore, it is common to carry out hot blast stove ****** of the magnetic toner ground for the purpose of raising the mobility of magnetic toner, to fuse

the surface of magnetic toner, and to perform treatment taken a spherical shape. Although the mobility of magnetic toner itself improves by performing such processing, in order that magnetic toner may control and manufacture polarity and electrification quantity to an appropriate value by a charge controlling agent, the structure of the color as a charge controlling agent is complicated, It is lacking in stability, and decomposes or deteriorates at it from those, such as treatment temperature conditions in the time of heat kneading, a mechanical shock, and friction, It is influence of producing the phenomenon in which electrification controllability falls, or the outline part and surface part of a negative polarity toner having much conventional straight polarity magnetic particle powder, and the thickness of a resin coating layer becoming uneven etc., namely, the magnetic toner of reverse polarity and the mixing ratio of weak electrified toner particles increase. In order to consider it as magnetic toner excellent in improvement in imaging quality, fine line reproducibility, and story tonality, Since it is known that it is so effective that the diameter of a granule is used, it is necessary to make magnetic toner diameter[of a granule]-ize. It becomes a tendency which increases further and the standup of frictional electrification becomes blunt, the problem of an offset phenomenon, toner scattering, dirt inside the plane, etc., etc. occur, and the magnetic toner of reverse polarity and the mixing ratio of weak electrified toner particles become the big cause of reducing a picture characteristic. Therefore, as magnetic toner needed with an one-ingredient development system in order to reproduce a photograph faithfully, To meet a demand of a detailed latent image and fine line reproducibility, and story tonality, it can respond to improvement in the speed with the diameter of a granule, Although research of the magnetic toner which can respond and which has negative polarity with the diameter of a granule, and development are wholeheartedly considered by the severe demand of highly-efficient-izing of high-definition-izing etc., quality improvement, etc. and it is developed, what is still satisfied does not exist.

[0003]

[Objects of the Invention]Electrification quantity of this invention is also large at negative polarity, and an object of this invention is to provide magnetic particle powder and a manufacturing method for the same excellent also in the dispersibility in the inside of resin, or wettability.

MEANS

[Means for Solving the Problem]Particle shape and a surface state which are required of magnetic toner of negative polarity, this invention persons, A fault of an interaction between granular materials, such as a dispersion state between particles and character of a powder surface, is made solved, That manufacture of magnetic particle powder for magnetic toner which has negative polarity should be attained, Each pH value and silicon (Si) of a specific silicate A result of having examined coating weight and electrified polarity wholeheartedly, It has the characteristic suitable for magnetic toner of negative polarity, the knowledge of the manufacturing method of magnetic particle powder which has negative polarity with the sufficient wettability (binding capacity of magnetic particle powder and resin) of resin to magnetic powder particles and a dispersion state in inside of resin is carried out, and it came to complete this invention. That is, this invention is iron (Fe) to a particle surface. It receives and is silicon (Si). It carries out. 0.1-5.0 A silicon compound of weight % has adhered, And magnetic particle powder for magnetic toner, wherein electrification quantity is -60 - -10microc/g, After pH uses magnetite (Fe_3O_4) particle powder as 12 or more alkaline suspension, It is a manufacturing method of magnetic particle powder for magnetic toner adding a water-soluble silicon compound, making pH or less into eight after an appropriate time, and making a silicon compound adhere to the surface of the magnetic particle powder concerned. Silicon (Si) used for this invention Silicon (Si) It is used in a form of a compound, For example, it is not what can mention oxides, such as hydroxide, such as silicate, such as Na_2SiO_3 and Na_2SiO_5, and $Si(OH)_4$, and SiO_2, etc., and is limited to especially these, When the pH of solution is 12 or more, what is necessary is just water solubility.

[0005]

[Embodiment of the Invention]Hereafter, the manufacturing method of the magnetic particle powder about this invention is explained in full detail. Namely, the inside of the stirring type oxidation reaction tub of the wet type in which magnetic particle powder generally has a gas vent pipe, After heating the suspension containing the ferrous hydroxide

colloid produced by mixing a ferrous salt aqueous solution and an alkaline aqueous solution while nitrogen replaced at 70 to 100 **, It changes from nitrogen to oxygen containing gas, such as air, is manufactured by blowing gas, and is manufactured through processes, such as filtration, washing, desiccation, and grinding, after that by the conventional method. The particle shape generated by such a wet reaction turns into n face piece, an unfixed type, and spherical shape with the kind and quantity of the alkali solution used for neutralization.

[0006]After the ending reaction which made the magnetic particle generate by the above-mentioned method, and in pH 12 or more alkaline suspension, a water-soluble silicon compound (for example, specific silicate (Na_2O-$nSiO_2$)) – silicon (Si) content – iron (Fe) Receive. it becomes 0.1 to 5.0 % of the weight – quantity addition being carried out and, After carrying out stirring mixing for a while, the magnetic particle which should usually have straight polarity comes to show negative polarity according to making the pH value (pH 5 or less [pH eight or less preferably]) of the field made into the purpose with chloride adjust, and making a silicon component adhere to a magnetic particle surface part. When not carrying out pH adjustment even to this field, it is still a magnetic particle which has straight polarity. What is necessary is just to make the amount of silicon of a magnetic-particle-powder surface part increase, in order to enlarge negative band electrical quantity of the magnetic particle powder produced by performing it above. The making the coating weight of silicon in a specific silicate increase at this time purpose, a specific silicate is added in pH 12 or more [of an after / ending reaction] alkaline suspension, the divalent metal ion (Mn^{2+} and Co^{2+}.) after carrying out stirring mixing for a while Zn^{2+}, nickel^{2+}, Mg^{2+}, Cu^{2+}, etc., The pH value of the field which is independent, or targets the slurry solution of the system of reaction with a hydrochloric acid aqueous solution after carrying out stirring mixing in two or more kinds of combination may be made to adjust a water-soluble pigment agent, a coupling agent, etc., and a magnetic-particle-powder surface part may be made to carry out coprecipitation adhesion of the silicon. It does not limit in particular for those amount used. The magnetic particle powder which made the silicon component adhere to a magnetic-particle-powder surface part by such a method, considered it as the product of this invention through processes, such as filtration, washing, desiccation, and grinding, after that with the conventional method, and was manufactured turns into magnetic particle powder which has negative polarity.

[0007]The electrification quantity of the magnetic particle powder of this invention is -60 - -10microc/g, and is -50 - -15microc/g preferably, Since it is -50 - -20microc/g preferably and is the magnetic powder whose electrification quantity is [that the outline part and surface part of magnetic toner have negative band electrode nature] large, when it uses for magnetic toner, Neither reverse polarity nor weak electrified toner particles increase, a high developing characteristic will be acquired by being stabilized continuously, and a high-definition picture characteristic will be obtained. In this case, the target electrification quantity is not obtained on developer support as electrification quantity is more than -10microc/g, but the sharpness of the first stage to a picture worsens, and since it is lower than an appropriate range, image concentration serves as a thin picture with much fogging. The evil which it becomes easy to produce the so-called charge-up phenomenon of the magnetic toner which the electrification quantity of a developer is accumulated, becomes still larger, and checks proper electrification quantity by carrying out by repeating image output as it is less than -60microc/g, and produces the fall of image concentration gradually especially under damp low temperature environment occurs.

[0008]The measuring method of the electrification quantity of the magnetic particle powder of this invention is as follows. namely, – using the Toshiba Chemical CORP. make blowing off granular material electrification measuring device – first – a 100-ml poly bottle – the ferrite carrier 97.0g of Cu-Zn, and magnetic particle powder 3.0 g (3% of content), [put in and] Mixed elegance which rotated for 5 minutes and was made to DEBE-ize at 110 rpm Right weighing of the 0.2 g was carried out, and the electrification quantity of a value and a 30-second value was measured for 10 seconds by ** of nitrogen gas 1 kg/cm^2.

[0009]In the state of this magnetic particle powder and binding resin where it was kneaded, since magnetic powder is contained 30 to 80% of the weight to the whole magnetic toner, influence the performance of magnetic toner greatly, and. If the wettability (binding capacity of magnetic particle powder and resin) of resin to this magnetic particle powder and the dispersion state in the inside of resin are bad, in order to worsen the magnetic toner characteristic like the above, Although mobility was measured with the pouter tester device by Hosokawa Micron CORP. and the magnetic particle powder of this invention was converted into the weight per minute (g/min), Since mobility is also improving

rather than elegance conventionally, even if it makes it the small grain diameter toner needed for the demand of highly-efficient-izing or quality improvement, inside magnetic toner, Since the magnetic powder particles which have straight polarity are not used, magnetic particle powder with large electrification quantity is contained in the outline part and surface part of magnetic toner by negative polarity, Even if it produces the phenomenon in which decompose or deteriorate by the treatment temperature conditions in the time of heat kneading of the influence of the thickness of a resin coating layer becoming uneven etc., or the color as a charge controlling agent, a mechanical shock, friction, etc., and electrification controllability falls, From becoming easy [manufacturing process management], since the mixing ratio of reverse polarity or weak electrified toner particles does not increase, and excelling also in wettability or dispersibility. The magnetic action of magnetic toner each becomes uniform. As a result, even if it increases content, electrostatic property, image concentration, fogging, etc. and toner scattering will not be caused, and a clear copied image will be obtained. From being made to the diameter of a granule, magnetic toner can also follow enough a detailed latent image and fine line reproducibility, and story tonality, and can respond to improvement in the speed, and the magnetic toner which also meets the severe demand of highly-efficient-izing of high-definition-izing etc., quality improvement, etc. can be provided.

[0010]Dispersibility to the inside of resin of the magnetic particle powder which has the negative polarity of this invention, and magnetic toner evaluation were performed by the following method. namely, -- as magnetic powder 40 weight section and binder resin -- polyester resin (the product made from Kao Atlas.) After mixing enough molecular weight abbreviation 5000 59 weight section and carbon black (Mitsubishi Chemical make, MA-100) 1 weight section with a Henschel mixer together, Carry out melt kneading, carry out cooling solidification with a heating type biaxial mixer, and with a jet mill type grinder and a classifier. After obtaining the magnetic toner of the negative polarity which has the mean particle diameter of 10 micrometers, the magnetic distribution of this magnetic toner was measured by the following brush dispersing method about this magnetic toner using what improved the developing box of the commercial one component system copying machine. the brush dispersing method -- a mug -- when the number of rotations of a roller is improved at a variable ceremony and the charge of magnetic toner is made to fixed-ize, it is making number of rotations quick, and the toner with weak magnetism (magnetic material content -- few) is flown with a centrifugal force. By measuring the flown quantity and magnetism of the toner, it is the method of measuring the dispersibility of the magnetic powder in magnetic toner.

[0011]That is, since the above-mentioned brush dispersing method differs in the magnetic force of each magnetic toner when the dispersibility of the magnetic powder particles to the inside of resin is bad, it is an instrumentation method using magnetic toner with weak magnetic force being flown early. Measurement of toner scattering the suction pipe of PARTICLE COUNTER made from RION (KC-03 **** type particle counter), attaching to the developing box upper part for two ingredients, and putting in magnetic toner in a box -- a mug -- a roller being rotated violently and according to the centrifugal force by the rotation. As a result of attracting dust particles and measuring magnetic toner particle diameter and the number from the toner scattering atmosphere in a box, the amount of scattering (dust) of magnetic toner was a thing of ultralow volume.

[0012]As a result of carrying out various kinds of measurement using an aforesaid measuring method, the magnetic particle powder of this invention, In the state with binding resin for magnetic toner where it was kneaded, wettability (binding capacity of magnetic particle powder and resin) with resin and the dispersion state in the inside of resin are good, The content and the filling factor of magnetic particle powder become uniform, and magnetic toner with the diameter of a granule Reverse polarity, From the mixing ratio of weak electrified toner particles being very very small, and the electrification quantity of the standup of frictional electrification being well stable further. The clear copied image was obtained without reducing a picture characteristic, since the characteristic of imaging quality is raised, and there is also no toner scattering including copy image quality, resolution, image concentration, etc., and the problem of an offset phenomenon, dirt inside the plane, etc., etc. were prevented.

[0013]As the characteristic for which magnetic particle powder is asked, for the demand of highly-efficient-izing of magnetic toner used for various kinds of [in recent years] xerography systems, ** Although it is called for that the good thing (a toner characteristic becomes uniform) of dispersibility and ** saturation magnetization are large (the conveyance nature of magnetic toner is good), that ** residual magnetization is low (transfer nature is good), that **

black degree is large (image concentration is good), etc., Since the magnetic particle powder of this invention has polyhedral form (the shape of a ball also moving aside), its dispersibility is also good, Since magnetic shape anisotropy is small, holding power (Hc) is small, and in connection with it, residual magnetization (sigmar) is also small, The particle size distribution of this magnetic body for saturation magnetization (sigmas) being large magnetic particle powder, and also filling the aforementioned demand, it is good that it is 0.5 micrometer or less – holding power (Hc) becoming small too much, and, if 0.5 micrometer is exceeded. In connection with it, residual magnetization (sigmar) becomes still smaller, the tinting strength of what improving declines, if the content of magnetic particle powder is increased, a fixing defect will be started, picture nature and transfer nature will get worse, and dispersibility will worsen the whole characteristic. Therefore, it is desirable. It is at best especially preferred that it is 0.4-0.15 micrometer. It is good that they are 0.3-0, and 20 micrometers. Since residual magnetization (sigmar) also becomes still larger in connection with [become / holding power (Hc) / that it is under 0.15 micrometers or more / too much / large] it, Since distribution in binding resin becomes difficult and remains as an aggregate that it is easy to condense magnetic particle powder, inferior transfer and a fine line reproducibility fall arise, and high resolution is no longer obtained. About the determination of a particle size, it is required to provide the demand of highly-efficient-izing for which the magnetic toner for one ingredients by each manufacture is asked in the appropriate range filled enough.

EXAMPLE

[Example]Although an example and a comparative example are given and the manufacturing method of the magnetic particle powder of this invention is explained concretely hereafter, this invention is not limited to this. First, the details of the manufacturing method of the magnetic particle powder for magnetic toner used for this invention are explained. First, 4 l. of pure water is put in, aerating nitrogen gas in a stirring type oxidation reaction container with a capacity of 15 l. which has a gas vent pipe, It is a 3.33 mol/l. ferrous salt aqueous solution in it. 1.2 l. is added, It ranks second. 2.0 mol/l. sodium carbonate solution 2.8 l. adds, After adding 2.0 l. of 2.0 mol/l. caustic soda aqueous solutions after carrying out stirring mixing for 30 minutes and considering it as whole volume, temperature up was carried out to 90 **, stirring, it was filtered and washed, and was dried and the output which aerated the air of 1 l. / min for 8 hours, and was made was pulverized.

[0015]As a result of checking with the Akashi Factory scanning electron microscope (SEM) photograph, the shape of magnetic powder particles the number of fields of a particle surface, Particle diameter of an enlargement With the polyhedron magnetite particles which exist ten or more as a result of surveying each number of fields of 100 pieces (I counted the surface which is visible at this time, and thought that that back side was also the same). The mean particle diameter draws the parallel lines of prescribed width, after expanding a SEM photograph with a copy machine, and it is the particles on the line. The particle diameter (horizontal Ferre) of 150 pieces is measured visually, As a result of **(ing) particle diameter for magnification and considering it as a pitch diameter as a particle diameter value, at 0.23 micrometer. Magnetic properties are vibrating sample magnetometers (Toei Industry VSH-1 type). As a result of using and measuring, the holding power (Hc) in 5KOe (oersted) is 60 Oe (oersted), and saturation magnetic flux densities (sigmas) are 86.5 emu/g and a residual magnetic flux density (sigmar). It was 5.5 emu/g. Specific surface area was $5.8m^2/g$ as a result of measuring by the full automatic surface area measuring device multi-soap made from Yuasa Eye Onyx marble.

[0016]. Were obtained with the reaction method explained with the details of the manufacturing method of the magnetic particle powder of one to example 4 example. PH value which it has polyhedron particle shape in 12 or more ending reaction slurry solutions, receiving Fe_3O_4 in a sodium silicate solution – 1.25:2.5:5.0:10.0 wt% – it being made to add and, Stirring mixing is carried out for 15 minutes, and it is the above-mentioned reaction vessel. A 0.5N mol hydrochloric acid aqueous solution is added at the rate of 10 ml/min with a metering pump, and it is pH. Filter and wash it, it is dried, the sample adjusted to 8.0-5.0 is ground, and the processing condition and evaluation result which investigated electrification quantity, electrical resistance, and mobility are shown in Table 1. As shown in Table 1, it is silicon (Si) to iron (Fe). An increase of content checked that the electrification quantity of negative polarity increased.

[0017]PH value which has the polyhedron particle shape used for one to comparative example 2 Examples 1-4 stops addition of a sodium silicate solution in 12 or more ending reaction slurry solutions, and it is the last pH value. Other than having been referred to as 8.0 and 5.0, as a result of performing the same processing as the above, negative polarity was not shown.

[0018]The processing condition and evaluation result at this time are written together to Table 1.

[0019]

[Table 1]

	項　目	実施例1	実施例2	実施例3	実施例4	比較例1	比較例2
処理条件	スラリーPH	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量 (g)	50	50	50	50	50	50
	SiO_2添加量 (重量%)	1.25	2.50	5.00	10.0	無	無
	最終スラリーPH	8.0	5.0	5.0	5.0	8.0	5.0
	洗浄水 (市水,リットル)	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体
	Si/Fe付着量 (重量%)	0.76	0.98	1.29	3.95	極微量	極微量
	帯電量 (μc/g)						
	10sec	-16.0	-21.3	-25.8	-48.1	+13.3	+10.7
	30sec	-16.3	-21.0	-25.9	-49.0	+14.6	+11.0
	流動性(g/min)	18.6	21.6	27.6	24.4	13.4	17.0
	磁気特性 (1K Oe)						
	Hc	57	57	58	58	57	58
	σr	5.8	5.7	5.8	5.8	5.7	5.8
	σs	68.7	68.1	68.3	67.9	68.3	68.0
	電気抵抗 (Ω) 印加電圧 100V	1.3×10^{7}	6.8×10^{8}	4.5×10^{8}	3.7×10^{7}	9.2×10^{8}	6.8×10^{7}

[0020]PH value which it has the polyhedron particle shape used for five to example 9 Examples 1-4 in 12 or more ending reaction slurry solutions, receiving Fe_3O_4 in a sodium silicate solution 2.5wt% – the making the coating weight of silicon in a specific silicate increase (coprecipitation) purpose, after adding and carrying out stirring mixing for 15 minutes, a divalent metal ion (Mn^{2+}, Co^{2+}, Zn^{2+}, and nickel^{2+}.) After making the pigment agent and coupling agent of Mg^{2+}, Cu^{2+}, etc. and solution add and also carrying out stirring mixing for 15 minutes, a 0.5N mol hydrochloric acid aqueous solution to the above-mentioned reaction vessel with a metering pump. PH value It adjusts to 5.0 and grinds [filter, wash, dry and], and the processing condition and evaluation result which investigated electrification quantity, electrical resistance, and mobility are shown in Table 2. As shown in Table 2, when a divalent metal ion etc. and water-soluble pigment agent, and the coupling agent were added, the content of silicon (Si) began to increase to iron (Fe), and it was checked that electrification quantity also increases. Those sulfate, a chloride, a nitrate, etc. can be mentioned as a divalent metal ion source.

[0021]As a result of performing the same processing as the above except having stopped addition of the sodium silicate solution by three to comparative example 4 Examples 5-9, the polarity of magnetic particle powder did not change from positive to negative. It is written together to Table 2 that an evaluation result is a processing condition at

this time. As the above-mentioned example showed, all in an ending reaction slurry solution a sodium silicate solution, In order to become the magnetic particle powder in which negative polarity is shown as a result of filtering, washing, drying and cracking and measuring electrification quantity, after making PH value into an acid side by chloride neutralization, and to enlarge electrification quantity, What is necessary is just to make the amount of silicon of the outline part of magnetic particle powder, or a surface part increase, and a divalent metallic ion, a water-soluble pigment agent, a coupling agent, etc. may be added, and silicon may be made to coprecipitate further.

[0022]

[Table 2]

	項　目	実施例5	実施例6	実施例7	実施例8	実施例9	比較例3	比較例4
処理条件	スラリーPH	12.5	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量 (g)	50	50	50	50	50	50	50
	SiO_2添加量 (重量%)	2.50	2.50	2.50	2.50	2.50	無	無
	$MnCl_2$(重量%)	1.00	無	無	無	無	1.00	無
	$ZnCl_2$(重量%)	無	1.00	無	無	無	無	無
	$MgCl_2$(重量%)	無	無	1.00	無	無	無	1.00
	顔料　分散剤 (重量%)	無	無	無	1.00	無	無	無
	カップリング剤 (重量%)	無	無	無	無	1.00	無	無
	最終スラリーPH	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	洗　浄　水 (市水,リットル)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体	多面体
	Si／Fe付着量 (重量%)	1.07	1.06	0.96	0.91	1.05	極微量	極微量
	帯電量 (μc/g)							
	10sec	-22.2	-20.3	-23.9	-29.0	-30.4	+7.4	+1.1
	30sec	-22.6	-21.7	-25.3	-31.2	-31.4	+7.9	+1.2
	流動性(g/min)	22.8	23.8	20.4	24.3	25.0	13.9	13.0
	電気抵抗 (Ω) 印加電圧 100V	1.1×10^{7}	5.2×10^{7}	5.6×10^{7}	3.8×10^{7}	3.0×10^{8}	3.5×10^{8}	5.8×10^{7}

CORRECTION OR AMENDMENT

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[Written amendment]
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[Amendment 1]
[Document to be Amended]Specification
[Item(s) to be Amended]Claim
[Method of Amendment]Change
[The contents of amendment]
[Claim(s)]
[Claim 1]
To a particle surface, it is iron (Fe). Magnetic particle powder for magnetic toner, wherein it received, and 0.1 to 5.0% of the weight of silicon (Si) has adhered, and electrification quantity is -60 - -10microc/g and mobility is 20.4 - 27.6 g/min.
[Claim 2]
A manufacturing method of the magnetic particle powder for magnetic toner according to claim 1 adding a water-soluble silicon compound, making pH or less into eight after an appropriate time, and making silicon adhere to the surface of the magnetic particle powder concerned after pH uses magnetite particle powder as 12 or more alkaline suspension.
[The amendment 2]
[Document to be Amended]Specification
[Item(s) to be Amended]0002
[Method of Amendment]Change
[The contents of amendment]
[0002]
[Description of the Prior Art]
The magnetic toner in which the development system of the dry type copying machines the conventional xerography, an electrostatic recording method, for electrostatic copiers, etc. has straight polarity is adopted widely. (5) for needlessness and (4) toner reinforcement with easy (3) concentration control with easy (2) maintenances with good (1) image reproducibility as a reason the one-ingredient development system by these dry type copying machine is adopted widely – it is because a compact and cheap developer is made.
However, if the intermediate color which what (reappearance of intermediate color) a photograph is faithfully reproduced for is needed, and is expressed by the difference in the density of a line does not always have the the same thickness of a line, the sharpness of imaging quality including fine line reproducibility, story tonality, resolution, image concentration, etc. will pose a problem especially in recent years.
Reappearance, resolution, etc. of story tonality satisfied the above-mentioned advanced demand, and made the stably same intermediate color the method which carries out a reappearance output, it changes to the conventional analog form, the thing using a digital latent image is developed, and the copying machine itself came to be written minutely [there is no latent image until now and]. As those copying machines, a laser beam printer (LBP), a digital printer (PPC), etc. are raised, These are selenium (Se). It is a thing using photo conductors, such as an organic photoreceptor (OPC)

of an amorphous silicon (a-Si) and right charge, and since such surface polarity has straight polarity, as for magnetic toner, the thing of a negative polarity toner is used. However, the magnetic powder particles used for these magnetic toner, Many generally have straight polarity and there is a problem referred to as having to control the strength (electrification quantity) of the polarity and polarity of magnetic toner to negative polarity in using it for the raw material for magnetic toner of negative polarity in manufacture of magnetic toner using a charge controlling agent.

In the manufacturing process of a toner, the manufacturing method of common magnetic toner Magnetic particle powder, After it dries the massive object which made carry out specified quantity mixing of binding resin, a charge controlling agent, the colorant, etc., and was acquired by carrying out melt kneading and mechanically ground means, such as a jet mill, grind (pulverizing method), usually it classifies and manufactures to the particles of a prescribed particle size. In order to manufacture negative magnetic toner at this time, polarity and electrification quantity are controlled and manufactured to an appropriate value by charge controlling agents, such as a metallic complex and azo dye.

However, as for conventional magnetic toner, particle shape and a surface state, the character of a powder surface, and the interaction between granular materials are regarded as questionable. for example, the wettability [on the state of magnetic particle powder and binding resin where it was kneaded, and as opposed to this magnetic powder particle] (binding capacity of magnetic particle powder and resin) of resin and the dispersion state in the inside of resin – it is bad (condensation). When ground by the above-mentioned grinding means, bordering on the portion on the surface of magnetic particle powder, or the part of a between [resin], separation cutting is carried out and it is ground in many cases (destructive cutting). If the dispersibility in the inside of resin and wettability manufacture using bad magnetic particle powder, the filling factor of magnetic powder material which receives per magnetic toner particle piece will not become uniform, but, as a result, variation will be produced in the magnetic action of magnetic toner each, and the inconvenience of reducing a developing characteristic will be produced. The surface where destructive cutting of the magnetic toner ground with pulverizing method was carried out has intense unevenness, therefore since the mobility of magnetic toner worsens, it is easy to produce the condensation and solidification between magnetic toner, and it becomes a cause by which the sharpness of imaging quality is missing, including fine line reproducibility, story tonality, resolution, copy density, etc. Therefore, it is common to carry out hot blast stove ****** of the magnetic toner ground for the purpose of raising the mobility of magnetic toner, to fuse the surface of magnetic toner, and to perform treatment taken a spherical shape.

Although the mobility of magnetic toner itself improves by performing such processing, in order that magnetic toner may control and manufacture polarity and electrification quantity to an appropriate value by a charge controlling agent, the structure of the color as a charge controlling agent is complicated, It is lacking in stability, and decomposes or deteriorates at it from those, such as treatment temperature conditions in the time of heat kneading, a mechanical shock, and friction, It is influence of producing the phenomenon in which electrification controllability falls, or the outline part and surface part of a negative polarity toner having much conventional straight polarity magnetic particle powder, and the thickness of a resin coating layer becoming uneven etc., namely, the magnetic toner of reverse polarity and the mixing ratio of weak electrified toner particles increase.

In order to consider it as magnetic toner excellent in improvement in imaging quality, fine line reproducibility, and story tonality, Since it is known that it is so effective that the diameter of a granule is used, it is necessary to make magnetic toner diameter[of a granule]-ize. It becomes a tendency which increases further and the standup of frictional electrification becomes blunt, the problem of an offset phenomenon, toner scattering, dirt inside the plane, etc., etc. occur, and the magnetic toner of reverse polarity and the mixing ratio of weak electrified toner particles become the big cause of reducing a picture characteristic.

Therefore, as magnetic toner needed with an one-ingredient development system in order to reproduce a photograph faithfully, To meet a demand of a detailed latent image and fine line reproducibility, and story tonality, it can respond to improvement in the speed with the diameter of a granule, Although research of the magnetic toner which can respond and which has negative polarity with the diameter of a granule, and development are wholeheartedly considered by the severe demand of highly-efficient-izing of high-definition-izing etc., quality improvement, etc. and it is developed (for example, JP,5-213620,A), what is still satisfied does not exist.

[Amendment 3]
[Document to be Amended]Specification
[Item(s) to be Amended]0004
[Method of Amendment]Change
[The contents of amendment]
[0004]
[Means for Solving the Problem]
Particle shape and a surface state which are required of magnetic toner of negative polarity, this invention persons, A fault of an interaction between granular materials, such as a dispersion state between particles and character of a powder surface, is made solved, That manufacture of magnetic particle powder for magnetic toner which has negative polarity should be attained, A result of having examined wholeheartedly each pH value of a specific silicate, coating weight of silicon (Si), and electrified polarity, It has the characteristic suitable for magnetic toner of negative polarity, the knowledge of the manufacturing method of magnetic particle powder which has negative polarity with the sufficient wettability (binding capacity of magnetic particle powder and resin) of resin to magnetic powder particles and a dispersion state in inside of resin is carried out, and it came to complete this invention.
That is, this invention is iron (Fe) to a particle surface. Received and 0.1 to 5.0% of the weight of silicon (Si) has adhered, And magnetic particle powder for magnetic toner, wherein electrification quantity is -60 - -10microc/g and mobility is 20.4 - 27.6 g/min, After pH uses magnetite (Fe_3O_4) particle powder as 12 or more alkaline suspension, It is a manufacturing method of the above-mentioned magnetic particle powder for magnetic toner adding a water-soluble silicon compound, making pH or less into eight after an appropriate time, and making silicon adhere to the surface of the magnetic particle powder concerned.
Silicon (Si) used for this invention Silicon (Si) It is used in a form of a compound, For example, it is not what can mention oxides, such as hydroxide, such as silicate, such as Na_2SiO_3 and Na_2SiO_5, and $Si(OH)_4$, and SiO_2, etc., and is limited to especially these, When the pH of solution is 12 or more, what is necessary is just water solubility.
[Amendment 4]
[Document to be Amended]Specification
[Item(s) to be Amended]0006
[Method of Amendment]Change
[The contents of amendment]
[0006]
After the ending reaction which made the magnetic particle generate by the above-mentioned method, and in pH 12 or more alkaline suspension, a water-soluble silicon compound (for example, specific silicate (Na_2O-$nSiO_2$)) – silicon (Si) coating weight – iron (Fe) Receive. it becomes 0.1 to 5.0 % of the weight – quantity addition being carried out and, After carrying out stirring mixing for a while, the magnetic particle which should usually have straight polarity comes to show negative polarity according to making the pH value (pH 5 or less [pH eight or less preferably]) of the field made into the purpose with chloride adjust, and making a silicon component adhere to a magnetic particle surface part. When not carrying out pH adjustment even to this field, it is still a magnetic particle which has straight polarity.
What is necessary is just to make the amount of silicon of a magnetic-particle-powder surface part increase, in order to enlarge negative band electrical quantity of the magnetic particle powder produced by performing it above. The making the coating weight of silicon in a specific silicate increase at this time purpose, a specific silicate is added in pH 12 or more [of an after / ending reaction] alkaline suspension, the divalent metal ion (Mn^{2+} and Co^{2+}.) after carrying out stirring mixing for a while Zn^{2+}, nickel^{2+}, Mg^{2+}, Cu^{2+}, etc., The pH value of the field which is independent, or targets the slurry solution of the system of reaction with a hydrochloric acid aqueous solution after carrying out stirring mixing in two or more kinds of combination may be made to adjust a water-soluble pigment agent, a coupling agent, etc., and a magnetic-particle-powder surface part may be made to carry out coprecipitation adhesion of the silicon. It does not limit in particular for those amount used. The magnetic particle powder which made the silicon component adhere to a magnetic-particle-powder surface part by such a method, considered it as the product of this invention through processes, such as filtration, washing, desiccation, and grinding, after that with the conventional method, and was

manufactured turns into magnetic particle powder which has negative polarity.
[Amendment 5]
[Document to be Amended]Specification
[Item(s) to be Amended]0007
[Method of Amendment]Change
[The contents of amendment]
[0007]
The electrification quantity of the magnetic particle powder of this invention is -60 - -10microc/g, and is -50 - -15microc/g preferably, Since it is -50 - -20microc/g preferably and is the magnetic powder whose electrification quantity is [that the outline part and surface part of magnetic toner have negative band electrode nature] large, when it uses for magnetic toner, Neither reverse polarity nor weak electrified toner particles increase, a high developing characteristic will be acquired by being stabilized continuously, and a high-definition picture characteristic will be obtained.
In this case, the target electrification quantity is not obtained on developer support as electrification quantity is above -10microc/g, but the sharpness of the first stage to a picture worsens, and since it is lower than an appropriate range, image concentration serves as a thin picture with much fogging. The evil which it becomes easy to produce the so-called charge-up phenomenon of the magnetic toner which the electrification quantity of a developer is accumulated, becomes still larger, and checks proper electrification quantity by carrying out by repeating image output as it is less than -60microc/g, and produces the fall of image concentration gradually especially under damp low temperature environment occurs.
[Amendment 6]
[Document to be Amended]Specification
[Item(s) to be Amended]0009
[Method of Amendment]Change
[The contents of amendment]
[0009]
In the state of this magnetic particle powder and binding resin where it was kneaded, since magnetic powder is contained 30 to 80% of the weight to the whole magnetic toner, influence the performance of magnetic toner greatly, and. If the wettability (binding capacity of magnetic particle powder and resin) of resin to this magnetic particle powder and the dispersion state in the inside of resin are bad, in order to worsen the magnetic toner characteristic like the above, Although mobility was measured with the pouter tester device by Hosokawa Micron CORP. and the magnetic particle powder of this invention was converted into the weight per minute (g/min), mobility was also improving rather than elegance conventionally and the value became 20.4 - 27.6 g/min. Therefore, even if it makes it the small grain diameter toner needed for the demand of highly-efficient-izing or quality improvement, inside magnetic toner, Since the magnetic powder particles which have straight polarity are not used, magnetic particle powder with large electrification quantity is contained in the outline part and surface part of magnetic toner by negative polarity, Even if it produces the phenomenon in which decompose or deteriorate by the treatment temperature conditions in the time of heat kneading of the influence of the thickness of a resin coating layer becoming uneven etc., or the color as a charge controlling agent, a mechanical shock, friction, etc., and electrification controllability falls, Since it becomes easy [manufacturing process management] since the mixing ratio of reverse polarity or weak electrified toner particles does not increase, and it excels also in wettability or dispersibility, the magnetic action of magnetic toner each becomes uniform. As a result, even if it increases content, electrostatic property, image concentration, fogging, etc. and toner scattering will not be caused, and a clear copied image will be obtained. From being made to the diameter of a granule, magnetic toner can also follow enough a detailed latent image and fine line reproducibility, and story tonality, and can respond to improvement in the speed, and the magnetic toner which also meets the severe demand of highly-efficient-izing of high-definition-izing etc., quality improvement, etc. can be provided.
[Amendment 7]
[Document to be Amended]Specification
[Item(s) to be Amended]0013

[Method of Amendment]Change
[The contents of amendment]
[0013]
As the characteristic for which magnetic particle powder is asked, for the demand of highly-efficient-izing of magnetic toner used for various kinds of [in recent years] xerography systems, (1) Although it is called for that the good thing (a toner characteristic becomes uniform) of dispersibility and (2) saturation magnetization are large (the conveyance nature of magnetic toner is good), that (3) residual magnetization is low (transfer nature is good), that (4) black degrees are large (image concentration is good), etc., Since the magnetic particle powder of this invention has polyhedral form (the shape of a ball also moving aside), its dispersibility is also good, Since magnetic shape anisotropy is small, holding power (Hc) is small, and in connection with it, residual magnetization (sigmar) is also small, The particle size distribution of this magnetic body for saturation magnetization (sigmas) being large magnetic particle powder, and also filling the aforementioned demand, it is good that it is 0.5 micrometer or less – holding power (Hc) becoming small too much, and, if 0.5 micrometer is exceeded. In connection with it, residual magnetization (sigmar) becomes still smaller, the tinting strength of what improving declines, if the content of magnetic particle powder is increased, a fixing defect will be started, picture nature and transfer nature will get worse, and dispersibility will worsen the whole characteristic. Therefore, it is at best especially preferred that it is 0.4-0.15 micrometer preferably. It is good that it is 0.3-0.20 micrometer. Since residual magnetization (sigmar) also becomes still larger in connection with [become / holding power (Hc) / that it is below 0.15 micrometer / too much / large] it, Since distribution in binding resin becomes difficult and remains as an aggregate that it is easy to condense magnetic particle powder, inferior transfer and a fine line reproducibility fall arise, and high resolution is no longer obtained. About the determination of a particle size, it is required to provide the demand of highly-efficient-izing for which the magnetic toner for one ingredients by each manufacture is asked in the appropriate range filled enough.
[Amendment 8]
[Document to be Amended]Specification
[Item(s) to be Amended]0016
[Method of Amendment]Change
[The contents of amendment]
[0016]
The comparative example 1, Examples 1-3
. Were obtained with the reaction method explained with the details of the manufacturing method of the magnetic particle powder of an example. A pH value the magnetite particle powder which has polyhedron particle shape in 12 or more ending reaction slurry solutions, receiving Fe_3O_4 in a sodium silicate solution – 1.25:2.5:5.0:10.0 wt% – it being made to add and, Stirring mixing is carried out for 15 minutes, and it is the above-mentioned reaction vessel. A 0.5N mol hydrochloric acid aqueous solution is added at the rate of 10 ml/min with a metering pump, and it is pH. Filter and wash it, it is dried, the sample adjusted to 8.0-5.0 is ground, and the processing condition and evaluation result which investigated electrification quantity, electrical resistance, and mobility are shown in Table 1.
It is iron (Fe) as shown in Table 1. It receives and is silicon (Si). An increase of coating weight checked that the electrification quantity of negative polarity increased.
[Amendment 9]
[Document to be Amended]Specification
[Item(s) to be Amended]0017
[Method of Amendment]Change
[The contents of amendment]
[0017]
Comparative examples 2-3
A pH value the magnetite particle powder which has the polyhedron particle shape used for the comparative example 1 and Examples 1-3 in 12 or more ending reaction slurry solutions, Addition of a sodium silicate solution is stopped and it is the last pH value. Other than having been referred to as 8.0 and 5.0, as a result of performing the same processing

as the above, negative polarity was not shown.

[Amendment 10]

[Document to be Amended]Specification

[Item(s) to be Amended]0019

[Method of Amendment]Change

[The contents of amendment]

[0019]

[Table 1]

	項　目	比較例1	実施例1	実施例2	実施例3	比較例2	比較例3
処理条件	スラリー ｐＨ	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量 (g)	50	50	50	50	50	50
	SiO_2添加量 (重量%)	1.25	2.50	5.00	10.0	無	無
	最終スラリー ｐＨ	8.0	5.0	5.0	5.0	8.0	5.0
	洗　浄　水 (市水,ﾘｯﾄﾙ)	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体
	Si／Fe付着量 (重量%)	0.76	0.98	1.29	3.95	極微量	極微量
	帯電量 (μc/g)						
	10sec	-16.0	-21.3	-25.8	-48.1	+13.3	+10.7
	30sec	-16.3	-21.0	-25.9	-49.0	+14.6	+11.0
	流動性(g/min)	18.6	21.6	27.6	24.4	13.4	17.0
	磁気特性 (1K Oe)						
	Ｈｃ	57	57	58	58	57	58
	σｒ	5.8	5.7	5.8	5.8	5.7	5.8
	σｓ	68.7	68.1	68.3	67.9	68.3	68.0
	電気抵抗 (Ω) 印加電圧 100V	1.3×10^{7}	6.8×10^{8}	4.5×10^{8}	3.7×10^{7}	9.2×10^{6}	6.8×10^{7}

[Amendment 11]

[Document to be Amended]Specification

[Item(s) to be Amended]0020

[Method of Amendment]Change

[The contents of amendment]

[0020]
Examples 4-8
A pH value the magnetite particle powder which has the polyhedron particle shape used for the comparative example 1 and Examples 1-3 in 12 or more ending reaction slurry solutions, receiving Fe_3O_4 in a sodium silicate solution 2.5wt% – the making the coating weight of silicon in a specific silicate increase (coprecipitation) purpose, after adding and carrying out stirring mixing for 15 minutes, a divalent metal ion (Mn^{2+}, Co^{2+}, Zn^{2+}, and nickel^{2+}.) After making the pigment agent and coupling agent of Mg^{2+}, Cu^{2+}, etc. and solution add and also carrying out stirring mixing for 15 minutes, it is the above-mentioned reaction vessel. A 0.5N mol hydrochloric acid aqueous solution with a metering pump. PH value It adjusts to 5.0 and grinds [filter, wash, dry and], and the processing condition and evaluation result which investigated electrification quantity, electrical resistance, and mobility are shown in Table 2.
As shown in Table 2, when a divalent metal ion etc. and water-soluble pigment agent, and the coupling agent were added, the coating weight of silicon (Si) began to increase to iron (Fe), and it was checked that electrification quantity also increases. Those sulfate, a chloride, a nitrate, etc. can be mentioned as a divalent metal ion source.
[Amendment 12]
[Document to be Amended]Specification
[Item(s) to be Amended]0021
[Method of Amendment]Change
[The contents of amendment]
[0021]
Comparative examples 4-5
As a result of performing the same processing as the above except having stopped addition of the sodium silicate solution by Examples 4-8, the polarity of magnetic particle powder did not change from positive to negative. It is written together to Table 2 that an evaluation result is a processing condition at this time.
As the above-mentioned example showed, all in an ending reaction slurry solution a sodium silicate solution, In order to become the magnetic particle powder in which negative polarity is shown as a result of filtering, washing, drying and cracking and measuring electrification quantity, after making a pH value into an acid side by chloride neutralization, and to enlarge electrification quantity, What is necessary is just to make the amount of silicon of the outline part of magnetic particle powder, or a surface part increase, and a divalent metallic ion, a water-soluble pigment agent, a coupling agent, etc. may be added, and silicon may be made to coprecipitate further.
[Amendment 13]
[Document to be Amended]Specification
[Item(s) to be Amended]0022
[Method of Amendment]Change
[The contents of amendment]
[0022]
[Table 2]

	項　目	実施例4	実施例5	実施例6	実施例7	実施例8	比較例4	比較例5
処理条件	スラリーｐH	12.5	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量（g）	50	50	50	50	50	50	50
	SiO_2添加量（重量%）	2.50	2.50	2.50	2.50	2.50	無	無
	$MnCl_2$（重量%）	1.00	無	無	無	無	1.00	無
	$ZnCl_2$（重量%）	無	1.00	無	無	無	無	無
	$MgCl_2$（重量%）	無	無	1.00	無	無	無	1.00
	顔料　分散剤（重量%）	無	無	無	1.00	無	無	無
	カップリング剤（重量%）	無	無	無	無	1.00	無	無
	最終スラリーｐH	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	洗　浄　水（市水，リットル）	0.3	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体	多面体
	Si／Fe付着量（重量%）	1.07	1.06	0.96	0.91	1.05	極微量	極微量
	帯電量（μc/g）							
	10sec	-22.2	-20.3	-23.9	-29.0	-30.4	+7.4	+1.1
	30sec	-22.6	-21.7	-25.3	-31.2	-31.4	+7.9	+1.2
	流動性(g/min)	22.8	23.8	20.4	24.3	25.0	13.9	13.0
	電気抵抗（Ω）印加電圧 100V	1.1×10^{7}	5.2×10^{7}	5.6×10^{7}	3.8×10^{7}	3.0×10^{8}	3.5×10^{8}	5.8×10^{7}

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(54)【発明の名称】　磁性トナー用磁性粒子粉末及びその製造方法

(57)【要約】

【課題】　負極性で帯電量も大きく、樹脂中での分散性や濡れ性にも優れた、磁性トナー用磁性粒子粉末を提供する。

【解決手段】　粒子表面に、鉄（Fe）に対して珪素（Si）として 0.1～5.0重量％の珪素化合物が付着しており、且つ帯電量が－60～－10μc/ｇである磁性トナー用磁性粒子粉末。

【特許請求の範囲】
【請求項１】　粒子表面に、鉄（Fe）に対して珪素（Si）として 0.1～5.0重量％の珪素化合物が付着しており、且つ帯電量が－60～－10μc/ｇであることを特徴とする磁性トナー用磁性粒子粉末。
【請求項２】　マグネタイト粒子粉末をｐＨが12以上のアルカリ性懸濁液とした後、水溶性珪素化合物を添加し、しかる後ｐＨを８以下として当該磁性粒子粉末の表面に珪素化合物を付着させることを特徴とする磁性トナー用磁性粒子粉末の製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、電子写真法、静電記録法、静電複写法用等の一成分方式の現像に用いられる磁性トナー用の磁性粒子粉末及びその製造方法に関するものであり、さらに詳しくはデジタル潜像を用いた現像方式に使用される磁性トナー用として適した磁性粒子粉末及びその製造方法に関するものである。
【０００２】
【従来の技術及び発明が解決しようとする課題】従来の電子写真法、静電記録法、静電複写機用などの乾式複写機の現像方式は、正極性を有する磁性トナーが広く採用されている。これら乾式複写機による一成分現像方式が広く採用されている理由としては、①画像再現性が良好である、②メンテナンスが容易である、③濃度コントロールが不要、④トナー補強が容易である、⑤コンパクトで安価な現像装置ができるからである。しかし、近年は特に写真を忠実に再現する（中間調の再現）ことが必要とされ、線の密度の違いで表現する中間調は、常に線の太さが同じでないと、細線再現性や階調性、解像度や画像濃度等を含め、画像品質の鮮鋭さが問題となってくる。階調性の再現や解像度など、上記の高度な要求を満足させ、安定に同じ中間調を再現出力する方式として、複写機自体も従来のアナログ方式に変わり、デジタル潜像を用いたものが開発され、潜像が今までになく微細に書かれる様になった。それらの複写機としては、レーザープリンター（ＬＢＰ）、デジタルプリンター（ＰＰＣ）等があげられ、これらはセレン（Se）、アモルファスシリコン（a-Si)、正チャージの有機感光体（ＯＰＣ）等の感光体を用いたもので、これらの表面極性は正極性を有するため、磁性トナーは負極性トナーのものが用いられる。しかし、これらの磁性トナーに使用する磁性粉末粒子は、一般的に正極性を有しているものが多く、負極性の磁性トナー用原料に使用するには磁性トナーの製造において、荷電制御剤を用いて、磁性トナーの極性及び極性の強さ（帯電量）を負極性に制御しなければならないと言う問題がある。一般的な磁性トナーの製造方法は、トナーの製造工程において磁性粒子粉末、結着樹脂、荷電制御剤、着色剤等を所定量混合させ溶融混練し、得られた塊状体を乾燥し、ジェットミル等の機械的粉砕手段にて粉砕（粉砕法）した後、所定粒度の粒子に分級して製造するのが通常である。この時、負磁性トナーを製造するためには、金属錯塩、アゾ系染料等の荷電制御剤で極性や帯電量を適正値に制御して製造する。しかし、従来の磁性トナーは、粒子形状及び表面状態、粉体表面の性質、粉体間の相互作用が問題視されている。例えば、磁性粒子粉末と結着樹脂との混練された状態において、該磁性粉末粒子に対する樹脂の濡れ性（磁性粒子粉末と樹脂との結着力）や樹脂中での分散状態が悪い（凝集）と、上記粉砕手段で粉砕された場合、磁性粒子粉末表面の部分や樹脂間との部位を境界として、分離切断されて粉砕（破壊切断）される事が多い。また、樹脂中での分散性や濡れ性が悪い磁性粒子粉末を用いて製造すると、磁性トナー粒子一個あたりに対する、磁性粉末材料の充填率が均一にならず、その結果、磁性トナー個々の磁気作用にバラツキを生じ、現像特性を低下させるという不都合を生じる。さらに、粉砕法で粉砕された磁性トナーの破壊切断された表面は凹凸が激しく、そのため磁性トナーの流動性が悪くなることから、磁性トナー相互の凝集や固化が生じ易く、細線再現性や階調性、解像度、コピー濃度等を含め、画像品質の鮮鋭さに欠ける原因となる。そのため、磁性トナーの流動性を向上させることを目的として、粉砕した磁性トナーを熱風炉て処理し、磁性トナーの表面を溶融して、球形状にする処置を行っているのが一般的である。この様な処理を施すことにより、磁性トナー自体の流動性は改善されるものの、磁性トナーは荷電制御剤で極性や帯電量を適正値に制御して製造するため、荷電制御剤としての染料の構造は複雑で、安定性に乏しく、熱混練時での処理温度条件、機械的衝撃、摩擦等のより分解又は変質し、荷電制御性が低下する現象を生じたり、負極性トナーの外郭部及び表面部に、従来の正極性磁性粒子粉末が多く、また樹脂コート層の厚みが不均一化する等の影響で、即ち逆極性の磁性トナーや弱帯電トナー粒子の混合比率が増大する。更に、画像品質の向上や細線再現性、階調性に優れた磁性トナーとするには、小粒径にするほど有効であることが知られていることから、磁性トナーは小粒径化させる必要があり、逆極性の磁性トナーや弱帯電トナー粒子の混合比率はさらに増大する傾向となり、摩擦帯電の立ち上がりが鈍くなり、オフセット現象、トナー飛散、機内汚れ等の問題等が起き、画像特性を低下させる大きな原因となる。従って、一成分現像方式で、写真を忠実に再現するために必要とされる磁性トナーとして、小粒径で微細な潜像や細線再現性や階調性の要求に応え、且つ高速化に対応でき、高画質化等の高性能化や高品質化等の厳しい要求にも対応が可能な、小粒径で負極性を有する磁性トナーの研究、開発が鋭意検討され、且つ開発されているが未だ満足するものは存在していない。
【０００３】

【発明の目的】本発明は、負極性で帯電量も大きく、樹脂中での分散性や濡れ性にも優れた、磁性粒子粉末及びその製造方法を提供することを目的としている。

【０００４】

【課題を解決するための手段】本発明者らは、負極性の磁性トナーに要求される、粒子形状及び表面状態、粒子相互の分散状態、粉体表面の性質等の粉体間の相互作用の欠点を解決させ、更に、負極性を有する磁性トナー用磁性粒子粉末の製造を達成すべく、珪酸ナトリウムの各ｐＨ値と珪素（Si）の付着量、及び帯電極性について鋭意検討を行った結果、負極性の磁性トナーに適した特性を有し、磁性粉末粒子に対する樹脂の濡れ性（磁性粒子粉末と樹脂との結着力）や樹脂中での分散状態の良い、負極性を有する磁性粒子粉末の製造方法を知見し、本発明を完成するに至った。即ち本発明は、粒子表面に、鉄（Fe）に対して珪素（Si）として 0.1～5.0 重量％の珪素化合物が付着しており、且つ帯電量が－60～－10μc/ｇであることを特徴とする磁性トナー用磁性粒子粉末、さらに、マグネタイト（Fe_3O_4）粒子粉末をｐＨが12以上のアルカリ性懸濁液とした後、水溶性珪素化合物を添加し、しかる後ｐＨを８以下として当該磁性粒子粉末の表面に珪素化合物を付着させることを特徴とする磁性トナー用磁性粒子粉末の製造方法である。本発明に使用される珪素（Si）は、珪素（Si）化合物の形で用いられ、例えばNa_2SiO_3 、Na_2SiO_5 等の珪酸塩、$Si(OH)_4$ 等の水酸化物及びSiO_2等の酸化物等を挙げることができ、特にこれらに限定されるものではなく、水溶液のｐＨが12以上である場合に水溶性であるものであれば良い。

【０００５】

【発明の実施の形態】以下、本発明に関する磁性粒子粉末の製造方法について詳述する。即ち、一般的に磁性粒子粉末は、ガス通気管を有する湿式の攪拌式酸化反応槽内を、窒素で置換しながら第一鉄塩水溶液とアルカリ水溶液とを混合して得られた水酸化第一鉄コロイドを含む懸濁液を70～ 100℃に加熱後、窒素から空気等の酸素含有ガスに切り替えて、ガスを吹き込むことにより製造され、その後、常法により濾過、洗浄、乾燥、粉砕等の工程を経て製造されている。この様な湿式反応により生成する粒子形状は、中和に用いるアルカリ溶液の種類と量により、ｎ面体、不定型、球状形状となる。

【０００６】上記の方法で磁性粒子を生成させた反応終了後、ｐＨ12以上のアルカリ性懸濁液中に、水溶性珪素化合物（例えば珪酸ナトリウム（$Na_2O \cdot nSiO_2$））を、珪素（Si）の含有量が鉄（Fe）に対して 0.1～ 5.0重量％となる量添加して、しばらく攪拌混合させた後、塩酸にて目的とする領域のｐＨ値（ｐＨ８以下、好ましくはｐＨ５以下）に調節させ、磁性粒子表面部に珪素成分を付着させることで、通常は正極性を有すべき磁性粒子が、負極性を示すようになる。この領域にまでｐＨ調整をしない場合、正極性を有する磁性粒子のままである。上記の様にして得られる磁性粒子粉末の負帯電量を大きくするには、磁性粒子粉末表面部の珪素量を増加させれば良い。この時珪酸ナトリウム中の珪素の付着量を増加させる目的で、反応終了後のｐＨ12以上のアルカリ性懸濁液中に、珪酸ナトリウムを添加して、しばらく攪拌混合させた後、２価の金属イオン（Mn^{2+}、Co^{2+}、Zn^{2+}、Ni^{2+}、Mg^{2+}、Cu^{2+}等）や、水溶性の顔料分散剤やカップリング剤等を単独又は２種類以上の組合せで加え、更に攪拌混合させた後、反応系のスラリー溶液を塩酸水溶液にて、目的とする領域のｐＨ値に調節させて、磁性粒子粉末表面部に珪素を共沈付着させてもよい。また、それらの使用量については、特に限定するものではない。この様な方法で磁性粒子粉末表面部に珪素成分を付着させ、その後、常法により濾過、洗浄、乾燥、粉砕等の工程を経て本発明の製品とし、製造された磁性粒子粉末は、負極性を有している磁性粒子粉末となる。

【０００７】本発明の磁性粒子粉末の帯電量は－60～－10μc/ｇであり、好ましくは－50～－15μc/ｇであり、更に好ましくは－50～－20μc/ｇであることから、磁性トナー用に用いると磁性トナーの外郭部及び表面部は負帯電極性を有し、且つ、帯電量が大きい磁性粉末であるため、逆極性や弱帯電トナー粒子が増大することがなく、高い現像特性を連続的に安定して得られ、高画質の画像特性が得られることになる。この場合、帯電量が－10μc/ｇ以上であると、現像剤担持体上で目的とする帯電量が得られず、初期から画像の鮮鋭さが悪くなり、適正範囲よりも低いため画像濃度は薄くカブリの多い画像となる。また、－60μc/ｇ未満であると、画出しを繰り返し行うことで、現像剤の帯電量が蓄積され、更に大きくなり適正な帯電量を阻害するいわゆる磁性トナーのチャージアップ現象が生じ易くなり、特に低湿低温環境下で徐々に画像濃度の低下を生じる弊害が発生する。

【０００８】本発明の磁性粒子粉末の帯電量の測定方法は次の通りである。即ち、東芝ケミカル社製ブローオフ粉体帯電測定装置を用いて、まず 100mlのポリ瓶にCu－Znのフェライトキャリアー97.0ｇと磁性粒子粉末 3.0ｇ（含有率３％）を入れ、 110rpm で５分間回転させ、デベ化させた混合品 0.2ｇを正秤量し、窒素ガス１kg／cm^2 の圧で10秒値と30秒値の帯電量を測定した。

【０００９】また、該磁性粒子粉末と結着樹脂との混練された状態において、磁性粉末は磁性トナー全体に対して30～80重量％含有されているため、磁性トナーの性能を大きく左右すると共に、該磁性粒子粉末に対する樹脂の濡れ性（磁性粒子粉末と樹脂との結着力）や樹脂中での分散状態が悪いと前記の如く磁性トナー特性を悪くするため、本発明の磁性粒子粉末をホソカワミクロン（株）製のパウターテスター装置で流動性を測定し、１分当たりの重量に換算（ｇ／min)したが、流動性も従来品よりも向上していることから、高性能化や高品質化の要求に必要とされる小粒径トナーにしても、磁性トナー

内部には、正極性を有する磁性粉末粒子が使用されていないことから、磁性トナーの外郭部及び表面部に負極性で帯電量の大きい磁性粒子粉末が含まれており、樹脂コート層の厚みが不均一化するなどの影響や荷電制御剤としての染料の熱混練時での処理温度条件、機械的衝撃、摩擦等により分解又は変質し、荷電制御性が低下する現象を生じても、逆極性や弱帯電トナー粒子の混合比率が増大することもないことから製造工程管理も容易となり、且つ、濡れ性や分散性にも優れていることから、磁性トナー個々の磁気作用が均一となる。その結果、含有量を増しても、帯電性、画像濃度、カブリ等やトナー飛散を起こすことがなく、鮮明な複写画像が得られることになる。また、磁性トナーは小粒径に出来ることから、微細な潜像や細線再現性や階調性にも充分追従し且つ、高速化に対応でき、高画質化等の高性能化や高品質化等の厳しい要求にも応える磁性トナーを提供することができる。

【００１０】本発明の負極性を有する磁性粒子粉末の樹脂中への分散性や、磁性トナー評価は下記の方法により行った。即ち、磁性粉末40重量部と、バインダー樹脂としてポリエステル樹脂（花王アトラス（株）製、分子量約5000）59重量部、カーボンブラック（三菱化学（株）製、ＭＡ-100）１重量部を一緒に、ヘンシェルミキサーで充分混合したあと、加熱式２軸混合機にて溶融混練し、冷却固化させ、ジェットミル式粉砕機及び分級機で、平均粒径10μｍを有する負極性の磁性トナーを得た後、この磁性トナーについて、市販の一成分系複写機の現像ボックスを改良したものを用いて、次のブラシ飛散法により該磁性トナーの磁気分布を測定した。ブラシ飛散法とは、マグローラの回転数を可変式に改良し、磁性トナーの仕込み量を一定化させた場合、回転数を速くすることで、磁力の弱いトナー（磁性材含有量少ない）は、遠心力で飛ばされる。その飛ばされた量とそのトナーの磁気を測定することにより、磁性トナー中の磁性粉の分散性を計測する方法である。

【００１１】つまり、上記ブラシ飛散法は、樹脂中への磁性粉末粒子の分散性が悪い場合、個々の磁性トナーの磁気力が異なるため、磁気力の弱い磁性トナーが早く飛ばされることを利用した計測方法である。更に、トナー飛散の測定は、ＲＩＯＮ（株）製 PARTICLE COUNTER(ＫＣ-03 光散式粒子計数器）の吸入管を、二成分用現像ボックス上部に取り付け、ボックス内に磁性トナーを入れ、マグローラーを激しく回転させ、その回転による遠心力により、ボックス内のトナー飛散雰囲気より粉塵粒子を吸引し、磁性トナー粒径と個数を測定した結果、磁性トナーの飛散（粉塵）量は極微量のものであった。

【００１２】上記測定方法を用いて各種の測定をした結果、本発明の磁性粒子粉末は、磁性トナー用結着樹脂との混練された状態において、樹脂との濡れ性（磁性粒子粉末と樹脂との結着力）や樹脂中での分散状態が良く、磁性粒子粉末の含有量や充填率が均一となり、且つ、磁性トナーは小粒径ながら逆極性や、弱帯電トナー粒子の混合比率は極微少で更に、摩擦帯電の立ち上がりも良く帯電量も安定していることから、コピー画質や解像度、画像濃度等を含め、画像品質の特性を向上させ、且つ、トナー飛散もないことから、オフセット現象、機内汚れ等の問題等も防ぐことが出来ることから、画像特性を低下させることなく、鮮明な複写画像が得られた。

【００１３】更に、近年各種の電子写真法システムに用いられる、磁性トナーの高性能化の要求のため、磁性粒子粉末に求められる特性としては、①分散性の良いもの（トナー特性が均一になる）、②飽和磁化が大きいこと（磁性トナーの搬送性が良い）、③残留磁化が低いこと（転写性がよい）、④黒色度が大きいこと（画像濃度が良い）等が求められているが、本発明の磁性粒子粉末は多面体形状（球状もどき）を有するので分散性もよく、形状磁気異方性が小さいことから保持力（Ｈｃ）は小さく、それに伴い残留磁化（σｒ）も小さく、飽和磁化（σｓ）が大きい磁性粒子粉末であり、更に前記の要求を満たすための該磁性体の粒度分布は、0.5μｍ以下であることが良く、0.5μｍを越えると保持力（Ｈｃ）が小さくなりすぎ、それに伴い残留磁化（σｒ）が更に小さくなり分散性は向上するものの着色力が低下し、磁性粒子粉末の含有量を増やせば定着不良を起こし、画像性、転写性が悪化し全体特性を悪くすることになる。そのため、好ましくは 0.4～0.15μｍであることが良く、特に好ましくは 0.3～0,20μｍであることが良い。0.15μｍ以上下であると保持力（Ｈｃ）が大きくなりすぎ、それに伴い残留磁化（σｒ）も更に大きくなるので、磁性粒子粉末が凝集し易く結着樹脂中での分散が困難となり、凝集塊として残存することから転写不良や細線再現性の低下が生じ、高解像度が得られなくなる。更に粒度の決定については各製造による一成分用磁性トナーに求められる高性能化の要求を充分満たす適正範囲に定めることが必要である。

【００１４】

【実施例】以下、本発明の磁性粒子粉末の製造方法を、実施例及び比較例を挙げて具体的に説明するが、本発明はこれに限定されるものではない。先ず、本発明に使用した磁性トナー用磁性粒子粉末の製造方法の詳細について説明する。まず、ガス通気管を有する容量15リットルの攪拌式酸化反応容器に窒素ガスを通気しながら純水４リットルを入れ、その中に3.33mol/リットルの第一鉄塩水溶液 1.2リットルを加え、次いで 2.0mol/リットルの炭酸ソーダー水溶液を 2.8リットル添加し、30分攪拌混合した後、 2.0mol/リットルの苛性ソーダー水溶液を2.0リットル加えて全体液量とした後、攪拌しながら90℃に昇温させ、１リットル/minの空気を８時間通気して、出来た生成物を濾過、洗浄、乾燥、粉砕した。

【００１５】磁性粉末粒子の形状は、（株）明石製作所

製の走査型電子顕微鏡（ＳＥＭ）写真で確認した結果、粒子表面の面数は、拡大写真の粒径 100個のそれぞれの面数を実測（このとき見える表面を数え、その裏側も同じと考えた）した結果10以上ある多面体マグネタイト粒子で、その平均粒子径はＳＥＭ写真をコピー機で拡大したあと、所定幅の平行線を引きその線の上の粒子 150個の粒径（水平方向フェレ径）を目視にて計測し、粒径を倍率で除して粒径値として平均径とした結果、0.23μmで、磁気特性は振動試料型磁力計（東英工業ＶＳＨ-1型）を使用して測定した結果、５K0e（エルステッド）における保持力（Ｈｃ）が60 0e(エルステッド）で、飽和磁束密度（σｓ）は86.5 emu/g、残留磁束密度（σｒ） 5.5 emu/gであった。比表面積は、湯浅アイオニックス（株）製の全自動表面積測定装置マルチソープで測定した結果、5.8m²/g であった。

【００１６】実施例１～４

実施例の磁性粒子粉末の製造方法の詳細で説明した反応方法で得られた、多面体粒子形状を有するＰＨ値が12以上の反応終了スラリー溶液中に、珪酸ナトリウム水溶液をFe_3O_4 に対して1.25:2.5:5.0:10.0 wt％添加させ、15分間撹拌混合させ、上記反応槽に 0.5Ｎモルの塩酸水溶液を定量ポンプで10ml/minの速度で添加し、ｐＨを 8.0～5.0 に調整したサンプルを濾過、洗浄、乾燥、粉砕し、帯電量、電気抵抗、流動性を調査した処理条件及び評価結果を表１に示す。表１に示されるように、鉄（Ｆｅ）に対して珪素（Ｓｉ）の含有量が増加すると、負極性の帯電量が増すことが確認された。

【００１７】比較例１～２

実施例１～４に使用した多面体粒子形状を有するＰＨ値が12以上の反応終了スラリー溶液中に、珪酸ナトリウム水溶液の添加を中止し、最終ｐＨ値を 8.0と5.0 とした以外は上記と同様の処理を行った結果、負極性を示すことはなかった。

【００１８】この時の処理条件と評価結果を表１に併記する。

【００１９】

【表１】

	項　目	実施例1	実施例2	実施例3	実施例4	比較例1	比較例2
処理条件	スラリーPH	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量 (g)	50	50	50	50	50	50
	SiO_2添加量 (重量%)	1.25	2.50	5.00	10.0	無	無
	最終スラリーPH	8.0	5.0	5.0	5.0	8.0	5.0
	洗浄水 (市水,ﾘｯﾄﾙ)	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体
	Si／Fe付着量 (重量%)	0.76	0.98	1.29	3.95	極微量	極微量
	帯電量（μc/g）						
	10sec	-16.0	-21.3	-25.8	-48.1	+13.3	+10.7
	30sec	-16.3	-21.0	-25.9	-49.0	+14.6	+11.0
	流動性(g/min)	18.6	21.6	27.6	24.4	13.4	17.0
	磁気特性 (1K 0e)						
	Hc	57	57	58	58	57	58
	σr	5.8	5.7	5.8	5.8	5.7	5.8
	σs	68.7	68.1	68.3	67.9	68.3	68.0
	電気抵抗（Ω） 印加電圧 100V	1.3×10^{7}	6.8×10^{8}	4.5×10^{8}	3.7×10^{7}	9.2×10^{8}	6.8×10^{7}

【００２０】実施例５～９

実施例１～４に使用した多面体粒子形状を有するＰＨ値が12以上の反応終了スラリー溶液中に、珪酸ナトリウム水溶液をFe_3O_4 に対し 2.5wt％添加し、15分間撹拌混合させた後、珪酸ナトリウム中の珪素の付着量を増加（共沈）させる目的で、２価の金属イオン（Mn^{2+}、Co^{2+}、Zn

$^{2+}$、Ni^{2+}、Mg^{2+}、Cu^{2+}等）や水溶液の顔料分散剤やカップリング剤を添加させ、更に15分間撹拌混合させた後に、上記反応槽に 0.5Nモルの塩酸水溶液を定量ポンプで、ｐＨ値を 5.0に調整し、濾過、洗浄、乾燥、粉砕して、帯電量、電気抵抗、流動性を調査した処理条件及び評価結果を表２に示す。表２に示されるように、２価の金属イオン等や水溶性の顔料分散剤やカップリング剤を添加すると、鉄（Fe）に対して珪素（Si）の含有量は増加傾向となり、帯電量も増すことが確認された。また、２価の金属イオン源としては、それらの硫酸塩、塩化物、硝酸塩等を挙げることができる。

【００２１】比較例３～４

実施例５～９で、珪酸ナトリウム水溶液の添加を中止した以外は、上記と同様の処理を行った結果、磁性粒子粉末の極性は正から負に変化することはなかった。この時の処理条件と、評価結果を表２に併記する。上記実施例で示した如く、いずれも反応終了スラリー溶液中に、珪酸ナトリウム水溶液を、塩酸中和でＰＨ値を酸性サイドとした後、濾過、洗浄、乾燥、解砕し、帯電量を測定した結果、負極性を示す磁性粒子粉末となり、帯電量を大きくするには、磁性粒子粉末の外郭部や表面部の珪素量を増加させれば良く、更に、２価金属イオン、水溶性の顔料分散剤、カップリング剤等を添加して珪素を共沈させても良い。

【００２２】

【表２】

	項　目	実施例5	実施例6	実施例7	実施例8	実施例9	比較例3	比較例4
処理条件	スラリーPH	12.5	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量 (g)	50	50	50	50	50	50	50
	SiO_2添加量 (重量%)	2.50	2.50	2.50	2.50	2.50	無	無
	$MnCl_2$(重量%)	1.00	無	無	無	無	1.00	無
	$ZnCl_2$(重量%)	無	1.00	無	無	無	無	無
	$MgCl_2$(重量%)	無	無	1.00	無	無	無	1.00
	顔料　分散剤 (重量%)	無	無	無	1.00	無	無	無
	カップリング剤 (重量%)	無	無	無	無	1.00	無	無
	最終スラリー PH	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	洗　浄　水 (市水,リットル)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体	多面体
	Si／Fe付着量 (重量%)	1.07	1.06	0.96	0.91	1.05	極微量	極微量
	帯電量 (μc/g)							
	10sec	-22.2	-20.3	-23.9	-29.0	-30.4	+7.4	+1.1
	30sec	-22.6	-21.7	-25.3	-31.2	-31.4	+7.9	+1.2
	流動性(g/min)	22.8	23.8	20.4	24.3	25.0	13.9	13.0
	電気抵抗 (Ω) 印加電圧 100V	1.1×10^{7}	5.2×10^{7}	5.6×10^{7}	3.8×10^{7}	3.0×10^{8}	3.5×10^{8}	5.8×10^{7}

【公報種別】特許法第１７条の２の規定による補正の掲載
【部門区分】第６部門第２区分
【発行日】平成16年12月24日(2004.12.24)

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　Ｇ０３Ｇ　9/083
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　Ｇ０３Ｇ　9/08　３０１

【手続補正書】
【提出日】平成16年1月28日(2004.1.28)
【手続補正１】
【補正対象書類名】明細書
【補正対象項目名】特許請求の範囲
【補正方法】変更
【補正の内容】
【特許請求の範囲】
【請求項１】
粒子表面に、鉄（Fe）に対して0.1～5.0重量％の珪素（Si)が付着しており、且つ帯電量が－60～－10μc/ｇであり、流動性が20.4～27.6ｇ／minであることを特徴とする磁性トナー用磁性粒子粉末。
【請求項２】
マグネタイト粒子粉末をｐＨが12以上のアルカリ性懸濁液とした後、水溶性珪素化合物を添加し、しかる後ｐＨを８以下として当該磁性粒子粉末の表面に珪素を付着させることを特徴とする請求項１記載の磁性トナー用磁性粒子粉末の製造方法。
【手続補正２】
【補正対象書類名】明細書
【補正対象項目名】０００２
【補正方法】変更
【補正の内容】
【０００２】
【従来の技術及び発明が解決しようとする課題】
従来の電子写真法、静電記録法、静電複写機用などの乾式複写機の現像方式は、正極性を有する磁性トナーが広く採用されている。これら乾式複写機による一成分現像方式が広く採用されている理由としては、(1)画像再現性が良好である、(2)メンテナンスが容易である、(3)濃度コントロールが不要、(4)トナー補強が容易である、(5)コンパクトで安価な現像装置ができるからである。
しかし、近年は特に写真を忠実に再現する（中間調の再現）ことが必要とされ、線の密度の違いで表現する中間調は、常に線の太さが同じでないと、細線再現性や階調性、解像度や画像濃度等を含め、画像品質の鮮鋭さが問題となってくる。
階調性の再現や解像度など、上記の高度な要求を満足させ、安定に同じ中間調を再現出力する方式として、複写機自体も従来のアナログ方式に変わり、デジタル潜像を用いたものが開発され、潜像が今までになく微細に書かれる様になった。それらの複写機としては、レーザープリンター（ＬＢＰ）、デジタルプリンター（ＰＰＣ）等があげられ、これらはセレン（Se）、アモルファスシリコン（ａ-Si)、正チャージの有機感光体（ＯＰＣ）等の感光体を用いたもので、これらの表面極性は正極性を有するため、磁性トナーは負極性ト

ナーのものが用いられる。しかし、これらの磁性トナーに使用する磁性粉末粒子は、一般的に正極性を有しているものが多く、負極性の磁性トナー用原料に使用するには磁性トナーの製造において、荷電制御剤を用いて、磁性トナーの極性及び極性の強さ（帯電量）を負極性に制御しなければならないと言う問題がある。
一般的な磁性トナーの製造方法は、トナーの製造工程において磁性粒子粉末、結着樹脂、荷電制御剤、着色剤等を所定量混合させ溶融混練し、得られた塊状体を乾燥し、ジェットミル等の機械的粉砕手段にて粉砕（粉砕法）した後、所定粒度の粒子に分級して製造するのが通常である。この時、負磁性トナーを製造するためには、金属錯塩、アゾ系染料等の荷電制御剤で極性や帯電量を適正値に制御して製造する。
しかし、従来の磁性トナーは、粒子形状及び表面状態、粉体表面の性質、粉体間の相互作用が問題視されている。例えば、磁性粒子粉末と結着樹脂との混練された状態において、該磁性粉末粒子に対する樹脂の濡れ性（磁性粒子粉末と樹脂との結着力）や樹脂中での分散状態が悪い（凝集）と、上記粉砕手段で粉砕された場合、磁性粒子粉末表面の部分や樹脂間との部位を境界として、分離切断されて粉砕（破壊切断）される事が多い。また、樹脂中での分散性や濡れ性が悪い磁性粒子粉末を用いて製造すると、磁性トナー粒子一個あたりに対する、磁性粉末材料の充填率が均一にならず、その結果、磁性トナー個々の磁気作用にバラツキを生じ、現像特性を低下させるという不都合を生じる。さらに、粉砕法で粉砕された磁性トナーの破壊切断された表面は凹凸が激しく、そのため磁性トナーの流動性が悪くなることから、磁性トナー相互の凝集や固化が生じ易く、細線再現性や階調性、解像度、コピー濃度等を含め、画像品質の鮮鋭さに欠ける原因となる。そのため、磁性トナーの流動性を向上させることを目的として、粉砕した磁性トナーを熱風炉て処理し、磁性トナーの表面を溶融して、球形状にする処置を行っているのが一般的である。
この様な処理を施すことにより、磁性トナー自体の流動性は改善されるものの、磁性トナーは荷電制御剤で極性や帯電量を適正値に制御して製造するため、荷電制御剤としての染料の構造は複雑で、安定性に乏しく、熱混練時での処理温度条件、機械的衝撃、摩擦等のより分解又は変質し、荷電制御性が低下する現象を生じたり、負極性トナーの外郭部及び表面部に、従来の正極性磁性粒子粉末が多く、また樹脂コート層の厚みが不均一化する等の影響で、即ち逆極性の磁性トナーや弱帯電トナー粒子の混合比率が増大する。
更に、画像品質の向上や細線再現性、階調性に優れた磁性トナーとするには、小粒径にするほど有効であることが知られていることから、磁性トナーは小粒径化させる必要があり、逆極性の磁性トナーや弱帯電トナー粒子の混合比率はさらに増大する傾向となり、摩擦帯電の立ち上がりが鈍くなり、オフセット現象、トナー飛散、機内汚れ等の問題等が起き、画像特性を低下させる大きな原因となる。
従って、一成分現像方式で、写真を忠実に再現するために必要とされる磁性トナーとして、小粒径で微細な潜像や細線再現性や階調性の要求に応え、且つ高速化に対応でき、高画質化等の高性能化や高品質化等の厳しい要求にも対応が可能な、小粒径で負極性を有する磁性トナーの研究、開発が鋭意検討され、且つ開発されているが（例えば、特開平５－２１３６２０号公報）、未だ満足するものは存在していない。

【手続補正３】
【補正対象書類名】明細書
【補正対象項目名】０００４
【補正方法】変更
【補正の内容】
【０００４】
【課題を解決するための手段】
本発明者らは、負極性の磁性トナーに要求される、粒子形状及び表面状態、粒子相互の分散状態、粉体表面の性質等の粉体間の相互作用の欠点を解決させ、更に、負極性を有する磁性トナー用磁性粒子粉末の製造を達成すべく、珪酸ナトリウムの各ｐＨ値と珪素（Ｓｉ）の付着量、及び帯電極性について鋭意検討を行った結果、負極性の磁性トナーに適した特性を有し、磁性粉末粒子に対する樹脂の濡れ性（磁性粒子粉末と樹脂との結着力）や樹脂

中での分散状態の良い、負極性を有する磁性粒子粉末の製造方法を知見し、本発明を完成するに至った。
即ち本発明は、粒子表面に、鉄（Fe）に対して0.1～5.0重量％の珪素（Si)が付着しており、且つ帯電量が－60～－10μc/gであり、流動性が20.4～27.6g／minであることを特徴とする磁性トナー用磁性粒子粉末、さらに、マグネタイト（Fe_3O_4)粒子粉末をｐＨが12以上のアルカリ性懸濁液とした後、水溶性珪素化合物を添加し、しかる後ｐＨを８以下として当該磁性粒子粉末の表面に珪素を付着させることを特徴とする上記磁性トナー用磁性粒子粉末の製造方法である。
本発明に使用される珪素（Si）は、珪素（Si）化合物の形で用いられ、例えばNa_2SiO_3 、Na_2Si0_5 等の珪酸塩、$Si(OH)_4$ 等の水酸化物及びSiO_2等の酸化物等を挙げることができ、特にこれらに限定されるものではなく、水溶液のｐＨが12以上である場合に水溶性であるものであれば良い。
【手続補正４】
【補正対象書類名】明細書
【補正対象項目名】０００６
【補正方法】変更
【補正の内容】
【０００６】
上記の方法で磁性粒子を生成させた反応終了後、ｐＨ12以上のアルカリ性懸濁液中に、水溶性珪素化合物（例えば珪酸ナトリウム（$Na_20\cdot nSiO_2$））を、珪素（Si）の付着量が鉄（Fe）に対して 0.1～ 5.0重量％となる量添加して、しばらく攪拌混合させた後、塩酸にて目的とする領域のｐＨ値（ｐＨ８以下、好ましくはｐＨ５以下）に調節させ、磁性粒子表面部に珪素成分を付着させることで、通常は正極性を有すべき磁性粒子が、負極性を示すようになる。この領域にまでｐＨ調整をしない場合、正極性を有する磁性粒子のままである。
上記の様にして得られる磁性粒子粉末の負帯電量を大きくするには、磁性粒子粉末表面部の珪素量を増加させれば良い。この時珪酸ナトリウム中の珪素の付着量を増加させる目的で、反応終了後のｐＨ12以上のアルカリ性懸濁液中に、珪酸ナトリウムを添加して、しばらく攪拌混合させた後、２価の金属イオン（Mn^{2+}、Co^{2+}、Zn^{2+}、Ni^{2+}、Mg^{2+}、Cu^{2+}等）や、水溶性の顔料分散剤やカップリング剤等を単独又は２種類以上の組合せで加え、更に攪拌混合させた後、反応系のスラリー溶液を塩酸水溶液にて、目的とする領域のｐＨ値に調節させて、磁性粒子粉末表面部に珪素を共沈付着させてもよい。また、それらの使用量については、特に限定するものではない。この様な方法で磁性粒子粉末表面部に珪素成分を付着させ、その後、常法により濾過、洗浄、乾燥、粉砕等の工程を経て本発明の製品とし、製造された磁性粒子粉末は、負極性を有している磁性粒子粉末となる。
【手続補正５】
【補正対象書類名】明細書
【補正対象項目名】０００７
【補正方法】変更
【補正の内容】
【０００７】
本発明の磁性粒子粉末の帯電量は－60～－10μc/gであり、好ましくは－50～－15μc/gであり、更に好ましくは－50～－20μc/gであることから、磁性トナー用に用いると磁性トナーの外郭部及び表面部は負帯電極性を有し、且つ、帯電量が大きい磁性粉末であるため、逆極性や弱帯電トナー粒子が増大することがなく、高い現像特性を連続的に安定して得られ、高画質の画像特性が得られることになる。
この場合、帯電量が－10μc/gより上であると、現像剤担持体上で目的とする帯電量が得られず、初期から画像の鮮鋭さが悪くなり、適正範囲よりも低いため画像濃度は薄くカブリの多い画像となる。また、－60μc/g未満であると、画出しを繰り返し行うことで、現像剤の帯電量が蓄積され、更に大きくなり適正な帯電量を阻害するいわゆる磁性トナーの

チャージアップ現象が生じ易くなり、特に低湿低温環境下で徐々に画像濃度の低下を生じる弊害が発生する。

【手続補正６】
【補正対象書類名】明細書
【補正対象項目名】０００９
【補正方法】変更
【補正の内容】
【０００９】
また、該磁性粒子粉末と結着樹脂との混練された状態において、磁性粉末は磁性トナー全体に対して30～80重量％含有されているため、磁性トナーの性能を大きく左右すると共に、該磁性粒子粉末に対する樹脂の濡れ性（磁性粒子粉末と樹脂との結着力）や樹脂中での分散状態が悪いと前記の如く磁性トナー特性を悪くするため、本発明の磁性粒子粉末をホソカワミクロン（株）製のパウターテスター装置で流動性を測定し、１分当たりの重量に換算（ｇ／min)したが、流動性も従来品よりも向上しており、その値は20.4～27.6ｇ／minとなった。よって、高性能化や高品質化の要求に必要とされる小粒径トナーにしても、磁性トナー内部には、正極性を有する磁性粉末粒子が使用されていないことから、磁性トナーの外郭部及び表面部に負極性で帯電量の大きい磁性粒子粉末が含まれており、樹脂コート層の厚みが不均一化するなどの影響や荷電制御剤としての染料の熱混練時での処理温度条件、機械的衝撃、摩擦等により分解又は変質し、荷電制御性が低下する現象を生じても、逆極性や弱帯電トナー粒子の混合比率が増大することもないことから製造工程管理も容易となり、且つ、濡れ性や分散性にも優れていることから、磁性トナー個々の磁気作用が均一となる。その結果、含有量を増しても、帯電性、画像濃度、カブリ等やトナー飛散を起こすことがなく、鮮明な複写画像が得られることになる。また、磁性トナーは小粒径に出来ることから、微細な潜像や細線再現性や階調性にも充分追従し且つ、高速化に対応でき、高画質化等の高性能化や高品質化等の厳しい要求にも応える磁性トナーを提供することができる。

【手続補正７】
【補正対象書類名】明細書
【補正対象項目名】００１３
【補正方法】変更
【補正の内容】
【００１３】
更に、近年各種の電子写真法システムに用いられる、磁性トナーの高性能化の要求のため、磁性粒子粉末に求められる特性としては、(1)分散性の良いもの（トナー特性が均一になる）、(2)飽和磁化が大きいこと（磁性トナーの搬送性が良い）、(3)残留磁化が低いこと（転写性がよい）、(4)黒色度が大きいこと（画像濃度が良い）等が求められているが、本発明の磁性粒子粉末は多面体形状（球状もどき）を有するので分散性もよく、形状磁気異方性が小さいことから保持力（Ｈｃ）は小さく、それに伴い残留磁化（σｒ）も小さく、飽和磁化（σｓ）が大きい磁性粒子粉末であり、更に前記の要求を満たすための該磁性体の粒度分布は、 0.5μｍ以下であることが良く、 0.5μｍを越えると保持力（Ｈｃ）が小さくなりすぎ、それに伴い残留磁化（σｒ）が更に小さくなり分散性は向上するものの着色力が低下し、磁性粒子粉末の含有量を増やせば定着不良を起こし、画像性、転写性が悪化し全体特性を悪くすることになる。そのため、好ましくは 0.4～0.15μｍであることが良く、特に好ましくは 0.3～0.20μｍであることが良い。0.15μｍより下であると保持力（Ｈｃ）が大きくなりすぎ、それに伴い残留磁化（σｒ）も更に大きくなるので、磁性粒子粉末が凝集し易く結着樹脂中での分散が困難となり、凝集塊として残存することから転写不良や細線再現性の低下が生じ、高解像度が得られなくなる。更に粒度の決定については各製造による一成分用磁性トナーに求められる高性能化の要求を充分満たす適正範囲に定めることが必要である。

【手続補正８】

【補正対象書類名】明細書
【補正対象項目名】００１６
【補正方法】変更
【補正の内容】
【００１６】
比較例１、実施例１～３
実施例の磁性粒子粉末の製造方法の詳細で説明した反応方法で得られた、多面体粒子形状を有するマグネタイト粒子粉末をｐＨ値が12以上の反応終了スラリー溶液中に、珪酸ナトリウム水溶液をFe_3O_4 に対して1.25:2.5:5.0:10.0 wt％添加させ、15分間攪拌混合させ、上記反応槽に 0.5Ｎモルの塩酸水溶液を定量ポンプで10ml/minの速度で添加し、ｐＨを 8.0～5.0 に調整したサンプルを濾過、洗浄、乾燥、粉砕し、帯電量、電気抵抗、流動性を調査した処理条件及び評価結果を表１に示す。
表１に示されるように、鉄（Fe）に対して珪素（Si）の付着量が増加すると、負極性の帯電量が増すことが確認された。
【手続補正９】
【補正対象書類名】明細書
【補正対象項目名】００１７
【補正方法】変更
【補正の内容】
【００１７】
比較例２～３
比較例１、実施例１～３に使用した多面体粒子形状を有するマグネタイト粒子粉末をｐＨ値が12以上の反応終了スラリー溶液中に、珪酸ナトリウム水溶液の添加を中止し、最終ｐＨ値を 8.0と5.0 とした以外は上記と同様の処理を行った結果、負極性を示すことはなかった。
【手続補正１０】
【補正対象書類名】明細書
【補正対象項目名】００１９
【補正方法】変更
【補正の内容】
【００１９】
【表１】

	項　目	比較例1	実施例1	実施例2	実施例3	比較例2	比較例3
処理条件	スラリー ｐH	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量（g）	50	50	50	50	50	50
	SiO_2添加量（重量%）	1.25	2.50	5.00	10.0	無	無
	最終スラリー ｐH	8.0	5.0	5.0	5.0	8.0	5.0
	洗　浄　水（市水,ﾘｯﾄﾙ）	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体
	Si／Fe付着量（重量%）	0.76	0.98	1.29	3.95	極微量	極微量
	帯電量（μc/g）						
	10sec	-16.0	-21.3	-25.8	-48.1	+13.3	+10.7
	30sec	-16.3	-21.0	-25.9	-49.0	+14.6	+11.0
	流動性(g/min)	18.6	21.6	27.6	24.4	13.4	17.0
	磁気特性（1K Oe）						
	Hc	57	57	58	58	57	58
	σr	5.8	5.7	5.8	5.8	5.7	5.8
	σs	68.7	68.1	68.3	67.9	68.3	68.0
	電気抵抗（Ω）印加電圧 100V	1.3×10^{7}	6.8×10^{8}	4.5×10^{8}	3.7×10^{7}	9.2×10^{8}	6.8×10^{7}

【手続補正１１】
【補正対象書類名】明細書
【補正対象項目名】００２０
【補正方法】変更
【補正の内容】
【００２０】
実施例４～８
比較例１、実施例１～３に使用した多面体粒子形状を有するマグネタイト粒子粉末をｐＨ値が12以上の反応終了スラリー溶液中に、珪酸ナトリウム水溶液をFe_3O_4に対し 2.5wt%添加し、15分間攪拌混合させた後、珪酸ナトリウム中の珪素の付着量を増加（共沈）させる目的で、２価の金属イオン（Mn^{2+}、Co^{2+}、Zn^{2+}、Ni^{2+}、Mg^{2+}、Cu^{2+}等）や水溶液の顔料分散剤やカップリング剤を添加させ、更に15分間攪拌混合させた後に、上記反応槽に 0.5Ｎモルの塩酸水溶液を定量ポンプで、ｐＨ値を 5.0に調整し、濾過、洗浄、乾燥、粉砕し

て、帯電量、電気抵抗、流動性を調査した処理条件及び評価結果を表２に示す。
表２に示されるように、２価の金属イオン等や水溶性の顔料分散剤やカップリング剤を添加すると、鉄（Fe）に対して珪素（Si）の付着量は増加傾向となり、帯電量も増すことが確認された。また、２価の金属イオン源としては、それらの硫酸塩、塩化物、硝酸塩等を挙げることができる。
【手続補正１２】
【補正対象書類名】明細書
【補正対象項目名】００２１
【補正方法】変更
【補正の内容】
【００２１】
比較例４～５
実施例４～８で、珪酸ナトリウム水溶液の添加を中止した以外は、上記と同様の処理を行った結果、磁性粒子粉末の極性は正から負に変化することはなかった。この時の処理条件と、評価結果を表２に併記する。
上記実施例で示した如く、いずれも反応終了スラリー溶液中に、珪酸ナトリウム水溶液を、塩酸中和でｐＨ値を酸性サイドとした後、濾過、洗浄、乾燥、解砕し、帯電量を測定した結果、負極性を示す磁性粒子粉末となり、帯電量を大きくするには、磁性粒子粉末の外郭部や表面部の珪素量を増加させれば良く、更に、２価金属イオン、水溶性の顔料分散剤、カップリング剤等を添加して珪素を共沈させても良い。
【手続補正１３】
【補正対象書類名】明細書
【補正対象項目名】００２２
【補正方法】変更
【補正の内容】
【００２２】
【表２】

	項　目	実施例4	実施例5	実施例6	実施例7	実施例8	比較例4	比較例5
処理条件	スラリー ｐH	12.5	12.5	12.5	12.5	12.5	12.5	12.5
	スラリー中の Fe_3O_4量 (g)	50	50	50	50	50	50	50
	SiO_2添加量 (重量%)	2.50	2.50	2.50	2.50	2.50	無	無
	$MnCl_2$(重量%)	1.00	無	無	無	無	1.00	無
	$ZnCl_2$(重量%)	無	1.00	無	無	無	無	無
	$MgCl_2$(重量%)	無	無	1.00	無	無	無	1.00
	顔料　分散剤 (重量%)	無	無	無	1.00	無	無	無
	カップリング剤 (重量%)	無	無	無	無	1.00	無	無
	最終スラリー ｐH	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	洗　浄　水 (市水,ﾘｯﾄﾙ)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
評価結果	粒子形状	多面体	多面体	多面体	多面体	多面体	多面体	多面体
	Si／Fe付着量 (重量%)	1.07	1.06	0.96	0.91	1.05	極微量	極微量
	帯電量 (μc/g)							
	10sec	-22.2	-20.3	-23.9	-29.0	-30.4	+7.4	+1.1
	30sec	-22.6	-21.7	-25.3	-31.2	-31.4	+7.9	+1.2
	流動性(g/min)	22.8	23.8	20.4	24.3	25.0	13.9	13.0
	電気抵抗 (Ω) 印加電圧 100V	1.1×10^{7}	5.2×10^{7}	5.6×10^{7}	3.8×10^{7}	3.0×10^{8}	3.5×10^{6}	5.8×10^{7}